ISOTOPES

BY

F. W. ASTON, M.A., D.Sc., A.I.C., F.R.S.

FELLOW OF TRINITY COLLEGE, CAMBRIDGE

LONDON
EDWARD ARNOLD & CO.
1922

Printed in Great Britain

PREFACE

I HAVE undertaken the preparation of this book on Isotopes in response to many requests made to me by teachers of physics and chemistry and others working in these subjects that I should publish the results obtained by means of the Mass-spectrograph in a form more convenient to the public than that in which they first appeared. This is one of the reasons why the space allotted to the inactive isotopes may appear, in the light of the general title of the book, somewhat disproportionately large. Another is that the subject of radioactive isotopes really requires a book to itself, and I am in the hope that the inadequacy of my account may stimulate the production of such a volume by hands more competent than mine to deal with this very special and remarkable field of modern science. The logical order of exposition of a scientific subject is to start with the simple and from that build up the more complex. Unfortunately the sequence of events in experimental research is the exact opposite of this so that a compromise must be effected, unless one is content to sacrifice historical treatment altogether. The latter seems very undesirable in a new subject. I have endeavoured in Chapters I, II and IV, and elsewhere when possible, to adhere strictly to the historical order of events even at the cost of some reiteration.

I wish to take this opportunity of expressing my indebtedness to Mr. C. G. Darwin for his timely criticism and unfailing assistance throughout the work, and also to Mr. R. H. Fowler for help with the proofs. My thanks are also due to Professor Soddy for his diagram of the radioactive isotopes, to Mr. A. J. Dempster for kindly sending me the illustrations of his work, to the proprietors of the *Philosophical Magazine* and to the Council of the Chemical Society for permission to use the plates and figures of my original papers, and to Messrs. Macmillan & Co., for the diagram of the radioactive transformations.

F. W. ASTON.

CAMBRIDGE,
January, 1922.

CONTENTS

CHAPTER I

INTRODUCTION

CHAPTER II

THE RADIOACTIVE ISOTOPES

CHAPTER III

POSITIVE RAYS

CHAPTER IV

NEON

PAGE

CHAPTER V

THE MASS-SPECTROGRAPH

CHAPTER VI

ANALYSIS OF THE ELEMENTS

CHAPTER VII

ANALYSIS OF THE ELEMENTS (*Continued*)

CHAPTER VIII

THE ELECTRICAL THEORY OF MATTER

CHAPTER IX

ISOTOPES AND ATOMIC NUMBERS

CHAPTER X

The Spectra of Isotopes

CHAPTER XI

The Separation of Isotopes

LIST OF PLATES

CHAPTER I

INTRODUCTION

1. Introduction.—Towards the end of the last century the attitude of science in relation to the atomic theory started to undergo a complete and radical change. What had been before regarded as a convenient working hypothesis became with remarkable rapidity a definite statement of fact.

This transformation is now complete and in any well-equipped laboratory to-day not only can individual atoms be detected but the movements of the swiftest of them can be tracked and made visible even to the untrained eye.

The causes of this remarkable advance are to be ascribed in particular to the discovery of radioactivity, which has provided us with atomic projectiles possessing enough energy to produce visible and measurable effects individually, and in general to the steady and continuous improvement in technical methods. Subject to such unprecedented scrutiny it was to be expected that the fundamental physical theories which underlie the applied science of chemistry and form a solid mathematical foundation for its formulæ, might show hitherto unsuspected flaws. Such expectations began to be realised when, among the radioactive elements, Boltwood failed to separate ionium from thorium, and, among the inactive elements, when Sir J. J. Thomson a few years later observed the anomalous behaviour of neon when subjected to positive ray analysis. Further and still more delicate and careful scrutiny of these flaws revealed them, as it must always do, if they are real, not as fortuitous and disconnected but as a definite and ultimately intelligible pattern. It is with the interpretation of this pattern, so revealed, that this volume is concerned, so that it will be of interest to look back rather over a century to the beginning of the theories which form the background against which it was first observed.

2. Hypotheses of Dalton and Prout.—In the generalisation, known as the Atomic Theory, put forward by Dalton in 1803, which laid the foundations of the whole of modern chemistry, five postulates were laid down, and it is a striking tribute to the shrewd intuition of that observer that, of those five, to this day, the validity of one only is in any question. This postulate is that :—Atoms of the same element are similar to one another and equal in weight. It obviously consists of two parts and if we combine both as a definition of the word element the whole becomes a truism ; this aspect of the matter will be considered later on. For the present we shall take the word " element " to mean what Dalton evidently intended it to mean, and what we generally consider it to mean to-day, namely a substance such as chlorine or lead which has constant chemical properties, and which cannot be resolved into further components by any known chemical process. The first half —taken together with the other four postulates—is then sufficient to define the word " element " and the second becomes a pure hypothesis.

About ten years later Prout suggested that the atoms of the elements were all made up of aggregations of atoms of hydrogen. On this view the weights of all atoms must be expressed as whole numbers, and if, as postulated by Dalton, the atoms of any particular element are all identical in weight, the atomic weights and combining ratios of all elements must be whole numbers also. Chemists soon found that in the case of many elements this was certainly not in agreement with experiment ; the more results they obtained the more impossible it was to express the atomic weights of *all* the elements as whole numbers. They therefore had to decide which hypothesis, Dalton's or Prout's, they would adopt. There was little doubt as to the result of the decision and in due course Prout's theory was abandoned.

It is interesting to consider the reasons which led to a decision which the subsequent history of science proves to have been as wise in principle as it was wrong in fact. The alternative views were—either an element was composed of atoms of identically the same weight, when in certain elements the weights of the individual atoms must be fractional, or these particular elements were composed of atoms of different weights mixed together, so that though the individual weights of the atoms would still be whole numbers their mean would be a fraction. It is almost inconceivable that the second alternative never occurred to philosophers during the time when the decision hung in the balance—indeed it was far more likely to be considered then than years later when Dalton's view had been generally accepted—but the objections to it were immediate and formidable. The idea that particles could behave in a practically identical manner even though they had different weights is not one that commends itself, *a priori*, to common sense, and as a working hypothesis for chemists it is as hopeless and indefinite as the simpler alternative is distinct and inspiring. Also it could be urged that the objections to the fractional weights of atoms were rather philosophic than practical. They were concerned with the structure of individual atoms and so might be, and wisely were, set aside till the time, distant enough it would then have seemed, when these hypothetical entities could be dealt with experimentally.

The idea that atoms of the same element are all identical in weight could not be challenged by chemical methods, for the atoms are by definition chemically identical and numerical ratios were only to be obtained in such methods by the use of quantities of the element containing countless myriads of atoms. At the same time it is rather surprising, when we consider the complete absence of positive evidence in its support that no theoretical doubts were publicly expressed until late in the nineteenth century, first by Schutzenberger and then by Crookes, and that these doubts have been regarded, even up to the last few years, as speculative in the highest degree. In order to dismiss the idea that the atoms of such a familiar element as chlorine might not all be of the same weight, one had only to mention diffusion experiments and the constancy of chemical equivalents. It is only within the last few years that the lamentable weakness of such arguments has been exposed and it has been realised that the experimental separation of atoms differing from each other by as much as 10 per cent. in weight, is really an excessively difficult operation.

3. Crookes' meta-elements.—The chemist who above all others urged the possibility of the heterogeneity of atoms was the late Sir William Crookes, to whom we are indebted for so many remarkable scientific prophecies. His address to the Chemical Section of the British Association at Birmingham in 1886[1] is a most amazing effort of reason and imagination combined and should be read by all those interested in the history of scientific thought. In it he says: "I conceive, therefore, that when we say the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on. We are here reminded of Newton's 'old worn particles.'

"Is it not possible, or even feasible, that these heavier and lighter atoms may have been in some cases subsequently sorted out by a process resembling chemical fractionation? This sorting out may have taken place in part while atomic matter was condensing from the primal state of intense ignition, but also it may have been partly effected in geological ages by successive solutions and reprecipitations of the various earths.

"This may seem an audacious speculation, but I do not think it beyond the power of chemistry to test its feasibility."

Later [2] he developed this idea in connection with his pioneer work on the rare earths. By a laborious process of fractional precipitation he subdivided the earth yttria into a number of components which had different phosphorescent spectra but resembled each other very closely in their chemical properties. Pointing out that at that time yttrium was considered to be an element he says: "Here, then, is a so-called element whose spectrum does not emanate equally from all its atoms; but some atoms furnish some, other atoms others, of the lines and bands of the compound spectrum of the element. Hence the atoms of this element differ probably in weight, and certainly

---

[1] *Nature*, **34**, 423, 1886.

[2] *Trans. Chem. Soc.*, **53**, 487, 1888; **55**, 257, 1889.

in the internal motions they undergo." He called such components "Meta-elements" and suggested that the idea might apply to the elements generally, for example referring to the seven series of bands in the absorption spectrum of iodine, "some of these molecules may emit some of the series, others others, and in the jumble of all these molecules, to which is given the name 'iodine vapour,' the whole seven series are contributors."

In so far as they differed a little in atomic weight and a mixture of them constituted a chemical element, these hypothetical meta-elements may be said to have offered the first feasible explanation of the fractional atomic weights. But as more and more refined chemical methods were applied, the rare earths one after another yielded to analysis and the different spectra observed by Crookes were shown to be due to the fact that he was dealing with a mixture of real elements, each of which had a characteristic spectrum and a definite atomic weight. The theory of meta-elements was therefore abandoned and the problem of fractional atomic weight remained unsolved.

4. The discovery of Isotopes.—As time went on the numbers representing the atomic weights grew more and more accurate and consistent. Significant figures one after another were added by one worker, confirmed by others, and finally approved by an International Committee. Small blame to the student therefore if, when studying the imposing list of numbers called the International Atomic Weights, he fell into the very natural error of confusing "atomic weights" with "weights of atoms," and considered that these figures did actually represent the relative weights of the individual atoms themselves.

Why so many of the atomic weights should be very nearly integers when expressed on the scale O = 16 was still a very difficult question to answer, for the probability against this being due to pure chance was enormous, but it was not until the discovery of radioactivity that the true reason for this curious jumble of whole numbers and fractions was suggested, and later confirmed generally by positive ray analysis. It is worth noting that the first experimental proof that the atoms of an element might be even approximately of the same weight was given by positive ray parabolas.[1]

The results given by the radioactive elements introduced a wealth of new and revolutionary ideas. One of these was that elements might exist which were chemically identical but yet differed in radioactive properties and even in atomic weight. By 1910 this idea had gained ground and was seriously put forward and discussed by Soddy. At about the same period the technique of positive ray analysis was rapidly being improved, and in 1912 the first results were obtained from neon which were later to support this new idea and carry it into the region of the non-radioactive elements. From this time onwards advances were made in the two fields side by side, and so it happened that at the meeting of the British Association in 1913[2] papers were read in different sections, one on the Radio-elements and the Periodic Law, the other on the Homogeneity of Neon, both of which tended to prove that substances could exist with identical, or practically identical, chemical and spectroscopic properties but different atomic weights.

The need for a specific name for such substances soon became imperative and Soddy suggested the word Isotopes (*ἴσος* equal, *τσπος*, place) because they occupied the same place in the periodic table of the elements.

---

[1] *V.* p. 29.

[2] Oddly enough this was the first meeting of the Association at Birmingham since the one twenty-seven years before at which Crookes made his prophetic remarks about atomic weights already quoted.

CHAPTER II

THE RADIOACTIVE ISOTOPES

5. Chemical identities among the radioactive elements.—Apart from the purely speculative considerations which have already been detailed, the theory of isotopes had its birth in the gigantic forward wave of human knowledge inaugurated by the discovery of radioactivity. It can admittedly be argued that, even if no radioactive elements existed, isotopes would inevitably have been discovered by the method of positive rays. But progress must then have been exceedingly slow, and the arrival at the real interpretation of the idea, depending as it does on Sir Ernest Rutherford's theory of the "nucleus" atom, almost impossible.

In 1906 Boltwood at Yale discovered a new element in the radioactive group which he called Ionium,[1] and described as having chemical properties similar to those of thorium. So much was this the case that if, by accident, salts of these two elements were mixed, he found it impossible to separate them again by any of the chemical processes.

Boltwood, being occupied in the experimental proof that ionium was the parent substance of radium, did not pursue this line of investigation further at the time, but the work was later taken in hand by Marckwald and Keetman of Berlin.[2] Thanks to the rapid advance in radioactive methods there were now at command means of detecting change in concentration of a delicacy unheard of in the previous work on the rare earths, but yet, after years of patient and laborious work, not the slightest sign of separation of ionium and thorium could be observed. The chemical similarity between these

---

[1] Boltwood, *Amer. J. Sci.*, **22**, 537, 1906; **24**, 370, 1907.

[2] Keetman, *Jahr. Radioactivitat*, **6**, 269, 1909.

two bodies was therefore of an order entirely different to that exhibited by the rare earth elements, and came as near absolute identity as the most critical mind could require.

This result was confirmed in the most rigorous manner by Auer v. Welsbach,[1] who was able to apply to the problem his valuable experience in work on the rare earths.

Furthermore, Mesothorium, discovered by Hahn in 1907, was shown to be chemically inseparable from radium by Marckwald [2] and Soddy [3] and similar chemical identities were shown to be exceedingly probable in many other cases of radioactive products. Certain regularities in the occurrence of these were pointed out by Hahn and Meitner.[4]

The situation was admirably summed up by Soddy in his report on radioactivity for the year 1910 [5] in the following words:—

"These regularities may prove to be the beginning of some embracing generalisation, which will throw light, not only on radioactive processes, but on elements in general and the Periodic Law. Of course, the evidence of chemical identity is not of equal weight for all the preceding cases, but the complete identity of ionium, thorium and radiothorium, of radium and mesothorium 1, of lead and radium D, may be considered thoroughly established. . . . The recognition that elements of different atomic weights may possess identical properties seems destined to have its most important application in the region of inactive elements, where the absence of a second radioactive nature makes it impossible for chemical identity to be individually detected. Chemical homogeneity is no longer a guarantee that any supposed element is not a mixture of several of different atomic weights, or that any atomic weight is not merely a mean number. The constancy of atomic weight, whatever the source of the material, is not a complete proof of homogeneity, for, as in the radioelements, genetic relationships might have resulted in an initial constancy of proportion between the several individuals, which no sub-

---

[1] A. von Welsbach, *Wien. Ber.* iia, **119,** 1011, 1910.

[2] Marckwald, *Ber. d. Chem. Ges.*, **40,** 3420, 1910.

[3] Soddy, *Trans. Chem. Soc.*, **99,** 72, 1911.

[4] Hahn and Meitner, *Physikal. Zeitsch.*, **11,** 493, 1910.

[5] Soddy, *Chem. Soc. Ann. Rep.*, 285, 1910.

sequent natural or artificial chemical process would be able to disturb. If this is the case, the absence of simple numerical relationships between the atomic weights becomes a matter of course rather than one of surprise."

6. Spectroscopic identity of isotopes.—The next great advance was of an even more revolutionary character. This consisted in the demonstration that the chemically indistinguishable products of the transformation of the radioactive elements might also be spectroscopically identical. The idea that elements of different atomic weight might yet have the same spectrum originated in Sir Ernest Rutherford's laboratory and appears to have been first entertained by A. S. Russell. With Rossi [1] he undertook the comparison between the spectrum of pure thorium and that of a mixture of thorium and ionium which radioactive evidence showed to contain a large percentage of the latter element. No new lines attributable to ionium were observed; in fact the spectra obtained were absolutely indistinguishable.

After giving in full the radioactive evidence as to the probable percentage of ionium present, and showing that it was practically impossible for this to be too small for its spectrum to appear, the writers go on as follows:—

"There are, however, two other possible ways of explaining our failure to obtain a distinct spectrum for ionium, besides the one discussed above. It is possible that:—

"(1) Ionium has no arc spectrum in the region investigated, or

"(2) Ionium and thorium have identical spectra in the region investigated.

"The first possibility is highly improbable, for all solids of high atomic weights have arc spectra, and, further, all rare earths have highly complicated spectra.

"The second possibility, though somewhat speculative in nature, is suggested by some recent work on the chemical properties of the radio-elements. There is no evidence at present to disprove its truth. It is well known that there are no less than four sets of longlived radio-elements, the

---

[1] Russell and Rossi, *Proc. Roy. Soc.*, 77A, 478, 1912.

members of each of which are chemically non-separable. These elements do not all belong to the group of rare earths, many non-radioactive members of which are known to be chemically very similar. Mesothorium, for instance, which is chemically non-separable from radium, belongs to the alkaline earth group. Again the two non-separable α ray products which are present in ordinary uranium, and which have been called by Geiger and Nuttall uranium I and uranium II belong to the chromium-molybdenum-tungsten group of elements. The explanation of these striking chemical similarities is very probably that the two very similar bodies are really different members of the same group of elements, the difference in their chemical properties being less pronounced than the difference between other members of the same group, owing to the small difference in their atomic weights. *But the possibility that they are identical in all physical and chemical properties, and differ only in atomic weight and in radioactive properties, should not be lost sight of. If this explanation should eventually prove justified, the spectrum of ionium would be identical with that of thorium.*"

It is not surprising that the idea was put forward with some caution. Unlike that of chemical identity which had been led up to by a gradual series of steps, it was entirely new and contrary to all the preconceived ideas of the relations between the spectrum of an element and the masses of its atoms. The new departure was supported by Soddy [1] but received some adverse criticism on the ground of insufficient evidence. The later work bearing on this point will be described in Chapter X.

Already in 1911 the theory of the "Nucleus Atom" [2] had been formulated. This gave the first hint as to the physical meaning of chemical and spectroscopic identity, namely that the nuclei of atoms might vary in their mass but yet, at the same time, possess some property in common with each other, namely nuclear charge, upon which the chemistry and spectra depend.

In 1912 appeared the electrochemical work of Hevesy,[3]

---

[1] Soddy, *Chem. News*, Feb. 28, 1913.

[2] *V.* p. 92.

[3] G. Hevesy, *Phil. Mag.*, **23**, 628, 1912; *Physikal. Zeitsch.* **15**, 672, 715, 1912.

which led to the discovery of the remarkable field of research opened up by the use of radioactive bodies as indicators.[1] A little later Paneth and Hevesy were able to show the complete identity of the electrochemical properties of Radium D and Lead.[2]

In 1914 Rutherford and Andrade [3] examined the self-excited X-ray spectrum of radium B. They used a crystal of rock salt for the analysis and got rid of the effect of the swift β rays by putting the source in a strong magnetic field. The wave length of the L radiation proved to be exactly that expected for lead from Moseley's experiment.[4] This was the first proof that isotopes had identical X-ray spectra. The actual values for ordinary lead were subsequently determined by Siegbahn and found to be in excellent agreement with Rutherford and Andrade's results.

7. The Chemical Law of Radioactive change.—This law, put in the briefest form, asserts: A radioactive element when it loses an alpha particle goes back two places in the Periodic Table; when it loses a beta particle it goes forward one place.

The law has been associated with the name of Soddy [5] who was the first to suggest, in the form of a valency property, that part of it relating to alpha rays.[6] But in its more complete enunciation, which took place early in 1913, at least four other investigators can claim a share.

Russell was the first to publish a law covering both kinds of rays,[7] but owing to the fact that he failed to realise that the sequence of elements in the periodic table is a continuous expression, his statement was not so simple and definite as it might have been. Fajans,[8] using as foundation the electrochemical

---

[1] *V.* p. 19.

[2] Paneth and Hevesy, *Sitzungber. K. Akad. Wiss. Wien*, iiA, **123**, 1037, 1913.

[3] Rutherford and Andrade, *Phil. Mag.* **27**, 854, 1914. [4] *V.* p. 93.

[5] *V.* Stewart, *Recent Advances in Physical and Inorganic Chemistry*, Longmans, 1919.

[6] Soddy, *The Chemistry of the Radio Elements*, 29, First Edition, Longmans, 1911.

[7] Russell, *Chem. News*, Jan. 31, 1913.

[8] Fajans, *Physikal. Zeitsch.* Feb. 15, 1913.

results of Hevesy,[1] and Soddy, working on the results of a very full chemical investigation carried out at his request by Fleck,[2] published the generalisation in its full and complete form independently, and practically at the same time.

This law, which will be shown later to be a natural consequence of the much wider generalisation discovered by Moseley,[3] has been of the greatest value in correlating the numerous products of radioactive change, and predicting with accuracy which of them will have identical properties. To the latter the name Isotopes was applied by Soddy in the following words: "The same algebraic sum of the positive and negative charges in the nucleus when the arithmetical sum is different gives what I call 'isotopes' or 'isotopic elements' because they occupy the same place in the periodic table. They are chemically identical, and save only as regards the relatively few physical properties which depend upon atomic mass directly, physically identical also." Any element which is the result of a series of changes involving the loss of twice as many beta particles as alpha particles must clearly be the isotope of the parent element, since it must inevitably, by the above law, reach the same place in the periodic table at the end of these operations.

8. Isobares.—Just as we can have elements of the same chemical properties but different atomic weight so we can also have those with the same atomic weight but different chemical properties. These Stewart[4] has called "Isobares." Any product due to the loss of a beta ray (which has a negligible mass)[5] must be an isobare of its parent substance, for, without change of mass, it has moved in the periodic table and so changed its chemical properties. It is interesting to note in this connection that no isobare has actually been discovered among the non-radioactive elements as yet, but they must certainly exist.[6]

---

[1] Hevesy, *Physikal. Zeitsch.* Jan. 15, 1913.

[2] Fleck, *Trans. Chem. Soc.* **103,** 381, 1052, 1913.

[3] *V.* p. 93.

[4] Stewart, *Phil. Mag.* **36,** 326, 1918.

[5] *V.* p. 91.

[6] *V.* p. 77.

9. The Radioactive Transformations.—The radioactive elements are all formed from the two parent elements uranium and thorium by a series of changes or transformations. These changes can be classified according to their nature into two types. In the first type of change called the α ray change the atom loses a particle of mass 4 carrying two positive charges ($+ 2e$) which has been identified with the nucleus of the helium atom.[1] In the second or β ray change the particle shot off has a negligible mass and carries a single negative charge ($- e$). Hence in an α ray change the element loses 4 units in atomic weight, while in a β ray change its weight is unaltered.

The rate of decay of an element is measured by the "half value" period which may vary from 10^{10} years to 10^{-11} of a second. The velocity with which the rays are ejected also varies and is apparently connected with the period of the element by the very interesting relation of Geiger and Nuttall.[2] The intricate researches by which the complex series of transformations have been explained belong to the subject of Radioactivity and cannot be described here. From the point of view of isotopes it will be enough to consider the final results which are given in the two diagrams (Figs. 1 and 2).

In the first of these, which is due to Soddy,[3] the nuclear charge or Atomic number,[4] upon which all the chemical and spectroscopic properties of the elements depend, and which expresses its position in the periodic table, is indicated by a series of columns edged with thick lines sloping downwards to the right. The atomic weights are shown by fine lines sloping in the opposite direction. The lines corresponding to even atomic weights have been omitted to simplify the scheme. All elements lying in the same column will therefore be *isotopes* and all elements lying on the same line sloping up to the right will be *isobares*. The α and β ray changes are shown by arrows and the period of decay of the elements indicated by times expressed in suitable units.

---

[1] *V*. Table p. 106.

[2] Rutherford, *Radioactive Substances and their Radiations*, p. 607, Cambridge, 1913.

[3] Soddy, *Trans. Chem. Soc.*, **115**, 16, 1919.

[4] *V*. p. 93.

FIG. 1.—Diagram of the transformations of the radio-elements showing atomic number, atomic weight and period of disintegration of each product.

The second diagram[1] is arranged in a simple manner to show the general chains of transformation at a glance. In it the α and β ray changes are plotted against atomic number and the other information omitted. On this diagram all elements lying on the same horizontal level will be isotopes. To take an example, uranium I which has an atomic number 92 and an atomic weight 238 loses one α particle and becomes uranium X, atomic number 90, atomic weight 234. This then gives off two β rays in succession, first becoming uranium X_2 and then Uranium II. Uranium II has an atomic number 92 so that it is an isotope of uranium I. It has an atomic weight 234 so it is an isobare of uranium X_1 and uranium X_2. Uranium II can disintegrate by shooting off an α particle in two different ways; about 8 per cent. of its atoms appear to form uranium Y, which is probably the parent substance of the actinium series. Disregarding this for the moment and following the main chain, 92 per cent. of the atoms of uranium

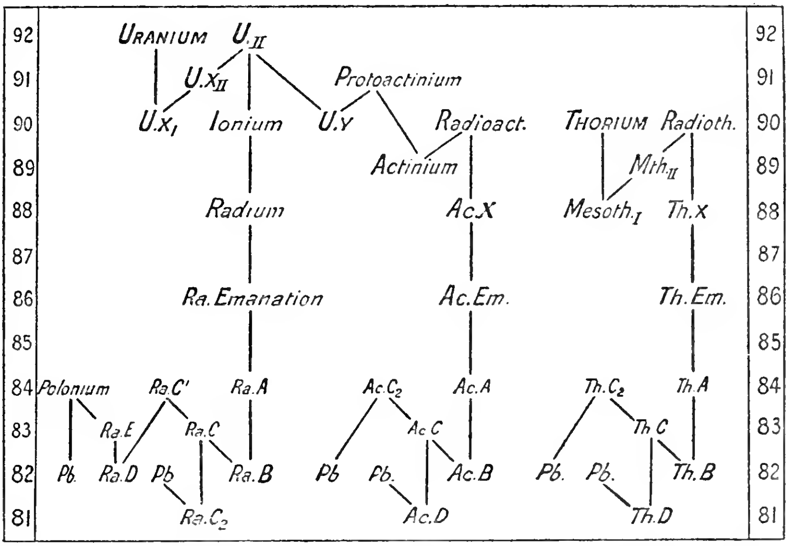


FIG. 2.—Diagram of the radioactive transformations in relation to atomic numbers. In every case a step two downwards is accompanied by the emission of an α particle and one downwards by a β particle.

---

[1] Darwin, *Nature*, **106**, 82, 1920.

II suffer an *α* ray change and are transformed into ionium, atomic weight 230, atomic number 90. Ionium loses an *α* particle and becomes radium, atomic weight 226. This by the same process changes to radium emanation, then to radium A, and then to radium B with atomic weight 214. We see that uranium II has lost 5 *α* particles in succession, thereby coming back 10 places, 92–82 in the periodic table, and its atomic weight has been reduced 20 units in the process. Radium B loses a *β* particle, becoming radium C which can disintegrate in two different ways. An extremely small proportion, 0·03 per cent., of its atoms undergo an *α* ray change to radium C_2 which then loses a *β* particle and may become inactive lead of atomic weight 210. The vast majority of the atoms of radium C lose a *β* particle and form radium C′. This next loses an *α* particle and becomes radium D, an active isotope of lead of atomic weight 210. Radium D now loses two *β* particles in succession, becoming radium E and then radium F, which is also called polonium. This finally undergoes its last *α* ray change and becomes inactive uranium lead of atomic weight 206.

The thorium and actinium chains can be followed on the diagrams in the same manner, but in the case of actinium the parent elements are not satisfactorily settled so that the atomic weights in this series are all doubtful.

10. The Atomic Weight of Lead.—The theory of Isotopes of which Professor Soddy had proved himself so prominent an advocate and defender, received its most triumphant vindication, as far as it concerned the products of radioactivity, at the hands of the very chemists who had most reason to doubt its general application, the specialists in the determination of atomic weights.

The charts of radioactive disintegration [1] show that the final product of every series is lead. If we take the main chain of the uranium-radium transformation this lead must have an atomic weight 206, for it has lost 5 alpha particles—each of weight 4—since it was radium, and the atomic weight of radium is 226. On the other hand if we take the main thorium chain

---

[1] P. 14.

the lead end product must be 6 alpha particles lighter than thorium (232·15) and so should have an atomic weight about 208.

Now ordinary lead, from non-radioactive sources has an atomic weight 207·20, so Soddy[1] suggested in 1913 that the lead derived from minerals containing uranium but no thorium might have a smaller atomic weight than ordinary lead, and on the other hand the atomic weight of lead from minerals containing thorium but no uranium might be greater.

The first experiments were made by Soddy and Hyman[2] with a very small quantity of lead from Ceylon Thorite. This gave a perceptibly higher atomic weight than ordinary lead. Later a large quantity of the same mineral was available. The lead from this when carefully purified gave a density 0·26 per cent. higher than that of common lead. On the assumption that the atomic volumes of isotopes are equal this figure corresponds to an atomic weight of 207·74. A chemical atomic weight determination gave 207·694. A sample of the same lead was sent to Vienna where Professor Honigschmid, a well known expert in such matters, obtained from it a value 207·77 as a mean of eight determinations. These figures not only showed that thorium lead had a higher atomic weight than ordinary lead but also that their atomic volumes were identical, as expected from theory.[3]

At the same time as this work was in progress, the leading American authority on atomic weights, T. W. Richards of Harvard, started a series of investigations on lead derived from various radioactive minerals.[4] The samples of lead from uranium minerals all gave results lower than ordinary lead, as was expected, and one particularly pure specimen of uraniolead from Norwegian cleveite gave 206·08,[5] a very striking agreement with theory. The following table of properties is taken from his Presidential address to the American Association at Baltimore, December, 1918.

---

[1] Soddy, *Ann. Rep. Chem. Soc.*, 269, 1913.

[2] Soddy and Hyman, *Trans. Chem. Soc.*, **105**, 1402, 1914.

[3] Soddy, *Roy. Ins.*, May 18, 1917.

[4] Richards and Lembert, *J. Amer. Chem. Soc.*, **36**, 1329, 1914.

[5] Richards and Wadsworth, *J. Amer. Chem. Soc.*, **38**, 2613, 1916.

	Common Lead.	Mixture Australian.	Uranio-Lead.	Percentage Difference.	
	A	B	C	A-B	A-C
Atomic weight	207·19	206·34	206·08	0·42	0·54
Density	11·337	11·280	11·273	0·42	0·56
Atomic volume	18·277	18·278	18·281	0·01	0·02
Melting point (absolute)	600·53	600·59	—	0·01	—
Solubility (of nitrate)	37·281	37·130	—	0·41	—
Refractive Index (nitrate)	1·7815	1·7814	—	0·01	—
Thermoelectric effect	—	—	—	0·00	—
Spectrum wave-length	—	—	—	0·00	0·00

In further confirmation Maurice Curie in Paris [1] reported 206·36 for a lead from carnotite, and a still lower figure, 206·046, was obtained by Honigschmid in Vienna for a lead from the very pure crystallised pitchblende from Morogoro. This is the lowest atomic weight found so far. The highest, 207·9, was also determined by Honigschmid for lead from Norwegian thorite.[2]

11. Atomic weights of Thorium and Ionium.—Although the above results obtained with lead are far the most conclusive and important it is not the only element which affords direct experimental evidence of the different atomic weights of isotopes. The atomic weight of ionium, calculated by adding the weight of one alpha particle to the atomic weight of its product, radium, is 230, whereas that of thorium, its isotope, is slightly above 232. Joachimsthal pitchblende contains hardly any thorium so that an ionium-thorium preparation separated by Auer von Welsbach from 30 tons of this mineral might be regarded as containing a maximum concentration of ionium. On the other hand the period of thorium is about 10^5 times longer than that of ionium so that it was doubtful if even in this preparation there would be enough ionium to show a difference in atomic weight. Honigschmid and Mlle. Horovitz have made a special examination of this point, first redetermining as accurately as possible the atomic weight of thorium and then that of the thorium-ionium prepar-

---

[1] M. Curie, *Compt. Rend.*, **158**, 1676, 1914.

[2] Honigschmid, *Zeit. Elektrochem.*, **24**, 163, 1918; **25**, 91, 1919.

ation from pitchblende. They found 232·12 for the atomic weight of thorium, and by the same careful method 231·51 for that of the thorium-ionium.

12. Use of radioactive isotopes as indicators.—Consider an inactive element A which has a radioactive isotope B. If these are mixed together in any proportions no chemical or physical process known is capable of altering the ratio of the proportions of this mixture to any measurable extent. Now the radioactive methods of detecting and measuring B are many millions of millions of times more delicate than the chemical methods of detecting and measuring A, so that by mixing with A a small quantity of B we can trace its presence far beyond the limits of chemical analysis. We have, as it were, marked the atoms of A with an indelible label so that the minutest trace of the element can be measured with ease and certainty.

By this powerful and novel device, which has been developed by G. Hevesy[1] 10^{-9} gr. of lead can be determined quantitatively and solution concentrations can be dealt with down to 10^{-14} of normal. By adding radium D to the lead salt and estimating it electroscopically the solubility of lead sulphide and chromate, and the amount of lead chloride carried down in a silver chloride precipitate, may readily be determined.

Recently, by the same principle, it has been shown that a free exchange of the metallic atom among the competing acid radicles occurs for ionised, but not for non-ionised, compounds. The general method was to mix solutions of two different compounds of lead in equimolecular proportions, the one compound only being "activated" by presence of thorium-B (which is isotopic with lead), and to determine the activity of the lead in the less soluble compound crystallising out. When active lead nitrate and inactive lead chloride are dissolved in molecular proportion in boiling pyridine, the lead in the lead chloride crystallising out is half as active as the lead in the original lead nitrate, but when such an active lead salt is so mixed with an organic compound of lead, such as lead tetraphenyl or diphenyl nitrate, in suitable solvents, no inter-

---

[1] Hevesy, Brit. Assoc., 1913; *Chem. News*, Oct. 13, 166, 1913.

change of lead occurs, and the active lead salt retains its original activity. This constitutes something like a direct proof of the ionic dissociation theory and of the current views as to the difference between the nature of chemical union in electrolytes and non-electrolytes. When the acetates of quadrivalent activated lead and of bivalent inactive lead are mixed in glacial acetic acid, the activity of the first compound, after crystallising out from the mixture, is reduced to one half. This indicates, since the two lead ions differ only by two electrons, a free interchange of electrons between them and a dynamic equilibrium between ions and electrons and between free electrons and the electrodes in electrolysis.[1]

Isotopes can also be used to determine the velocity of diffusion of molecules among themselves.[2] The rate of diffusion is dependent on the molecular diameter, and not on the mass, so that a radioactive element diffusing among the inactive molecules of its isotope affords a means of investigating this otherwise insoluble problem. The experiment has been tried with molten lead. At the bottom of a narrow vertical tube was placed a layer of lead rendered active by the presence of thorium-B, and above it a layer three times the height of common lead. The whole was kept at 340° for several days. After cooling, the cylinder was cut into four equal lengths, each melted and hammered into foil, and the concentration of thorium-B in each determined by alpha ray measurements. Values for the diffusion coefficient between 1·77 and 2·54 per sq. cm. per day, with a mean of 2·22 in seventeen experiments, were obtained. On certain theories of physical chemistry this corresponds with a diameter of the lead molecule between 0·78 and $1{\cdot}16 \times 10^{-8}$ cm., according to the formulae used to connect the two quantities. The value found by similar theories when reduced to a temperature of 18° and for a fluid of the viscosity of water, becomes 2·13. Since the value for lead ions diffusing in aqueous solutions is 0·68, this indicates that the molecular diameter in the case

---

[1] G. Hevesy and L. Zechmeister, *Ber.*, **53B**, 410, 1920; *Zeitsch. Elektrochem.* **26**, 151, 1920.

[2] J. Groh and Hevesy, *Ann. Physik.*, iv., **63**, 85, 1920.

of metallic lead is only a third of that in the case of the ion, and shows that the latter is probably hydrated.[1]

13. Classification of the radioactive isotopes.—It is clear that the relations between isotopes formed by radioactive disintegrations need not necessarily have the same simple form as those subsisting between isotopes of the inactive elements. Neuburger,[2] using the nucleus model of the radioelements proposed by Lise Meitner,[3] suggests that the radioactive isotopes may be divided into three or even four classes.

(1) Isotopes of the first class are those which possess only the same nuclear charge and the same arrangement of outer electrons such as radium and mesothorium I.

(2) Isotopes of the second class have, in addition, the same nuclear mass, that is to say the same atomic weight, and the same total number of nuclear "building stones." Examples of this class are ionium and uranium Y.

(3) Isotopes of the third class still possess the same number of each nuclear building stone, but they have a different arrangement of these in the atomic nucleus, and thus possess different chances of disintegrating, such as Radium D and Actinium B.

(4) Isotopes of the fourth class would be those possessing the same arrangement of nuclear building stones in the atomic nucleus, and thus the same probability of disintegrating. Such isotopes actually exist, but we have no available means of distinguishing between them. Hence we cannot at present designate them definitely as isotopes. Examples of these are radium C_2 and actinium D.

---

[1] Soddy, *Ann. Rep. Chem. Soc.*, 227, 1920.

[2] Neuburger, *Nature*, **108**, 180, 1921.

[3] Meitner, *Die Naturwissenschaften*, **9**, 423, 1921.

CHAPTER III

POSITIVE RAYS

14. Nature of Positive Rays.—Positive rays were discovered by Goldstein in 1886 in electrical discharge at low pressure. In some experiments with a perforated cathode he noticed streamers of light behind the perforations. This luminosity, he assumed, was due to rays of some sort which travelled in the opposite direction to the cathode rays and so passed through the apertures in the cathode, these he called "canalstrahlen." [1] Subsequently Wien showed that they could be deflected by a magnetic field.[2] They have been very fully investigated in this country by Sir J. J. Thomson,[3] who called them Positive Rays on account of the fact that they normally carry a charge of positive electricity.

The conditions for the development of the rays are, briefly, ionisation at low pressure in a strong electric field. Ionisation, which may be due to collisions or radiation, means in its simplest case the detachment of one electron from a neutral atom. The two resulting fragments carry charges of electricity of equal quantity but of opposite sign. The negatively charged one is the electron, the atomic unit of negative electricity itself,[4] and is the same whatever the atom ionised. It is extremely light and therefore in the strong electric field rapidly attains a high velocity and becomes a cathode ray. The remaining fragment is clearly dependent on the nature of the atom ionised. It is immensely more massive than the electron, for

---

[1] Goldstein, *Berl. Ber.*, **39**, 691, 1886.

[2] Wien, *Verh. d. Phys. Gesell.*, 17, 1898.

[3] J. J. Thomson, *Rays of Positive Electricity and their Application to Chemical Analyses*, Longmans, Green, 1913.

[4] R. A. Millikan, *The Electron*, University Chicago Press, 1918.

the mass of the lightest atom, that of hydrogen, is about 1845 times that of the electron, and so will attain a much lower velocity under the action of the electric field. However, if the field is strong and the pressure so low that it does not collide with other atoms too frequently it will ultimately attain a high speed in a direction opposite to that of the detached electron, and become a "positive ray." The simplest form of positive ray is therefore an atom of matter carrying a positive charge and endowed, as a result of falling through a high potential, with sufficient energy to make its presence detectable. Positive rays can be formed from molecules as well as atoms, so that it will at once be seen that any measurement of their mass will give us direct information as to the masses of atoms of elements and molecules of compounds, and that this information will refer to the atoms or molecules *individually*, not, as in chemistry, to the mean of an immense aggregate. It is on this account that the accurate analysis of positive rays is of such importance.

In order to investigate and analyse them it is necessary to obtain intense beams of the rays. This can be done in several ways. The one most generally available is by the use of the discharge in gases at low pressure.

15. Mechanism of the electric discharge in gases at low pressure.—It is a somewhat striking anomaly that while the working of the very recently invented "Coolidge" X ray bulb can be simply described and explained, this is far from being the case with the much older ordinary "gas" tube. Notwithstanding the immense amount of research work done on the discharge at low pressure its most obvious phenomena are well nigh entirely lacking explanation. Modern measurements and other data have merely destroyed the older theories, without, as yet, giving others to replace them.

For the purposes of describing positive rays it is not necessary to consider such puzzles as the "striated discharge" or other phenomena connected with the anode end of the tube, but some ideas as to what is going on near the cathode will be a considerable help in our interpretation of the results of positive ray analysis, and vice versa.

16. The Crookes Dark Space.—The comparatively dimly lit space in front of the cathode, terminating at the bright "negative glow" was first observed by Crookes. Its length is roughly inversely proportional to the pressure of the gas in the tube. Its boundary the edge of the negative glow is remarkably sharp in most gases, quite amazingly so in pure oxygen. If large plane cathodes are used so that the effect of the glass walls—up to now a complete mystery—is minimised very accurate and consistent measurements can be obtained. Such measurements have been made under a great variety of conditions by the writer.[1] The distribution of electric force in the dark space has also been determined for large plane electrodes [2] but no theory yet put forward can account for the numerical relations obtained in these investigations, nor for others obtained later with perforated electrodes.[3]

One can, however, be fairly certain that ionisation is going on at all points throughout the dark space, and that it reaches a very high intensity in the negative glow. This ionisation is probably caused for the most part by electrons liberated from the surface of the cathode (Cathode Rays). These, when they reach a speed sufficient to ionise by collision, liberate more free electrons which, in their turn, become ionising agents, so that the intensity of ionisation from this cause will tend to increase as we move away from the cathode. The liberation of the original electrons from the surface of the cathode is generally regarded as due to the impact of positive ions (Positive Rays) generated in the negative glow and the dark space, but this idea, for which there is a fair amount of definite evidence, is now called in question by some recent experiments of Ratner.[4]

In addition to cathode ray ionisation the positive rays travelling towards the cathode themselves are capable of ionising the gas, and radiation may also play an important part in the same process. The surface of the cathode will

---

[1] Aston, *Proc. Roy. Soc.* **79A,** 80, 1907; Aston and Watson, *ibid.* **86A,** 168, 1912; Aston, *ibid.* **87A,** 428, 437, 1912.

[2] Aston, *Proc. Roy. Soc.* **84A,** 526, 1911.

[3] Aston, *Proc. Roy. Soc.* **96A,** 200, 1919.

[4] Ratner, *Phil. Mag.* **40,** 795, 1920.

therefore be under a continuous hail of positively charged particles. Their masses may be expected to vary from that of the lightest atom to that of the heaviest molecule capable of existence in the discharge tube, and their energies from an indefinitely small value to a maximum expressed by the product of the charge they carry × the total potential applied to the electrodes. The latter is practically the same as the fall of potential across the dark space. If the cathode be pierced the rays pass through the aperture and form a stream heterogeneous both in mass and velocity which can be subjected to examination and analysis.

17. Methods of detecting positive rays.—The glow caused by the passage of the rays through rarefied gas led to their original discovery but is not made use of in accurate work. For visual effects the rays are best detected by a screen made of powdered willemite, which glows a faint green when bombarded by them. When permanent effects are required this screen is replaced by a photographic plate. The sensitivity of the plate to positive rays bears no particular relation to its sensitivity to light, and so far the best results have been obtained from comparatively slow " process " plates of the type known as " Half-Tone." The real relative intensities of rays of different mass cannot be compared by screens or photographic plates, except in the possible case of isotopes of the same element ; they can only be determined reliably by collecting the rays in a Faraday cylinder and measuring their total electric charge.

18. Sir J. J. Thomson's " Parabola " method of analysis.—The method by which Sir J. J. Thomson made such a complete investigation into the properties of positive rays, and which still remains pre-eminent in respect to the variety of information it supplies, consists essentially in allowing the rays to pass through a very narrow tube and then analysing the fine beam so produced by electric and magnetic fields.

The construction of one of the types of apparatus used is indicated in Fig. 3. The discharge by which the rays are made takes place in a large flask A similar to an ordinary X-ray bulb of about $1\frac{1}{2}$ litres capacity. The cathode B is placed in the neck of the bulb. Its face is made of aluminium, and so shaped that it presents to the bulb a hemispherical front provided in the centre with a funnel-shaped depression. This hole through which the rays pass is continued as an extremely fine-bore tube, usually of brass, about 7 cms. long, mounted in a thick iron tube forming the continuation of the cathode as indicated. The finer the bore of this tube the more accurate are the results obtained, and tubes have been made with success as narrow as one-tenth of a millimetre, but as the intensity of the beam of rays falls off with the inverse fourth power of the diameter a practical limit is soon reached. The cathode is kept cool during the discharge by means of the water-jacket C.

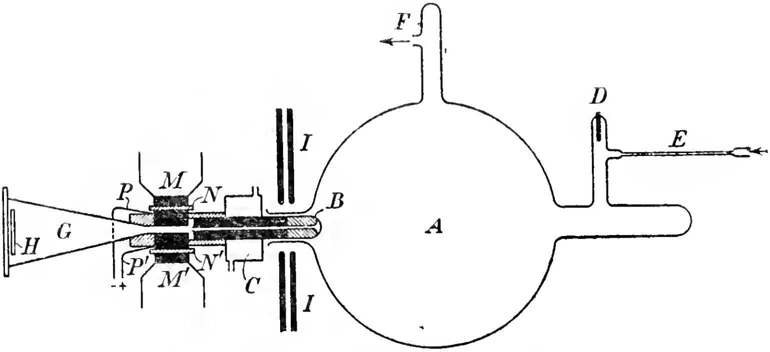


Fig. 3.—Positive Ray Apparatus

The anode is an aluminium rod D, which is generally placed for convenience in a side tube. In order to ensure a supply of the gas under examination a steady stream is allowed to leak in through an exceedingly fine glass capillary tube E, and after circulating through the apparatus is pumped off at F by a Gaede rotating mercury pump. By varying the speed of the pump and the pressure in the gas-holder communicating with E, the pressure in the discharge tube may be varied at will and maintained at any desired value for considerable lengths of time. The pressure is usually adjusted so that the discharge potential is 30,000 to 50,000 volts. During the discharge all the conditions necessary for the production of positive rays are present in A. Under the influence of the enormous potentials they attain high speeds as they fly towards the cathode, and those falling axially pass right through the fine tube, emerging as a narrow beam.

This beam is subjected to analysis by causing it to pass between the pieces of soft iron P, P′ which are placed between the poles M, M′ of a powerful electromagnet. P and P′ constitute the pole pieces of the magnet, but are electrically insulated from it by thin sheets of mica N, N′, and so can be raised to any desired potential difference by means of the leads shown in the diagram. The rays then enter the highly exhausted "camera" G, and finally impinge upon the fluorescent screen or photographic plate H. In order that the stray magnetic field may not interfere with the main discharge in A, shields of soft iron, I, I′ are interposed between the magnet and the bulb.

If there is no field between the plates P, P′ the beam of rays will strike the screen at a point in line with the fine tube called the undeflected spot. If an electric field of strength X is now applied between the plates a particle of mass m, charge e, moving with velocity v, will be deflected in the plane of the paper and will no longer strike the screen at the undeflected spot, but at a distance x from it. Simple dynamics show that if the angle of deflection is small $x = k(\mathrm{X}e/mv^2)$. In the same way, if the electric field is removed and a magnetic field of strength H applied between P and P′ the particle will be deflected at right angles to the plane of the paper and strike the screen at a distance y from the undeflected spot where $y = k'(\mathrm{H}e/mv)$, k and k' being constants depending solely on the dimensions and form of the apparatus used. If now, with the undeflected spot as origin, we take axes of co-ordinates OX, OY along the lines of electric and magnetic deflection, when both fields are applied simultaneously the particle will strike the screen at the point (x, y) where y/x is a measure of its velocity and y^2/x is a measure of m/e its ratio of mass to charge.

Now e can only exist as the electronic charge $4{\cdot}77 \times 10^{-10}$ C.G.S. or a simple multiple of it. Thus if we have a beam of positive rays of constant mass, but moving with velocities varying over a considerable range, y^2/x will be constant and the locus of their impact with the screen will be a parabola *pp′* (Fig. 4). When other rays having a larger mass *m′* but the same charge are introduced into the beam, they will appear as another parabola *qq′* having a smaller magnetic displacement. If any straight line *p*, *q*, *n* be drawn parallel to the magnetic axis OY cutting the two parabolas and the electric axis OX in *p*, *q*, *n* it will be seen at once that $m'/m = pn^2/qn^2$. That is to say, the masses of two or more particles can be compared directly by merely measuring lengths the ratio of which is entirely independent of the form of the apparatus and the experimental conditions.

This is really the fundamental principle upon which the method is based. A photographic record is obtained on which we can identify at least one parabola as being associated with atoms or molecules of known mass; all the other parabolas can then be measured and compared with this one and their masses deduced. With electric and magnetic fields roughly known there is little difficulty in such an identification, and to make quite sure the absolute value of *m/e* for the hydrogen atom was determined and found to agree with the values obtained by other methods. In actual practice, since OX is an imaginary line and has no existence on the photograph, in order that the measurements may be made with greater convenience and accuracy the magnetic field is reversed during the second half of the exposure, when—in the case we are considering—two new parabolas will appear at *rr′*, *ss′*, due to *m* and *m′* respectively; the masses can now be compared by the equation $m'/m = pr^2/qs^2$: *p*, *q*, *r*, *s* being any straight line cutting the curves approximately parallel to the magnetic axis. The measurement of these lengths is independent of zero determination, and if the curves are sharp can be carried out with considerable accuracy.

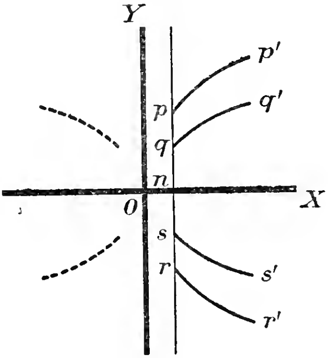
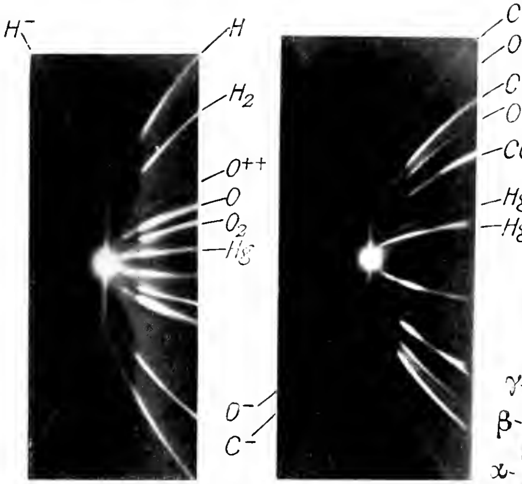
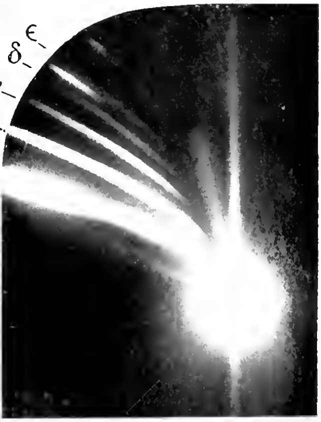


FIG. 4.—Positive Ray Parabolas.



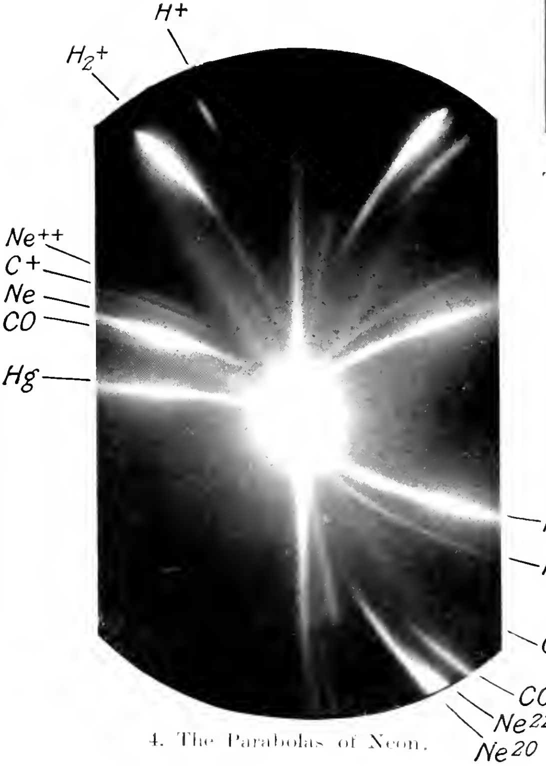
1. 2.

Photographs of Typical Positive Ray Parabolas.

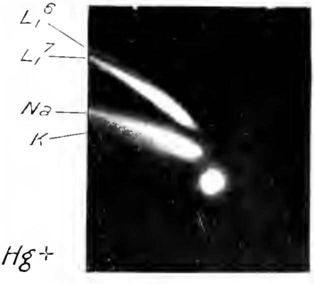


3.

The Multiply Charged Parabolas of Mercury



4. The Parabolas of Neon.



5.

The Parabolas of Lithium.

Some of the photographic results obtained by this method of analysis are shown in Plate I. The fact that the streaks are definite sharp parabolas, and not mere blurs, was the first experimental proof that the atoms of the same element had very approximately the same mass.

It has been shown that the electrical displacement is in inverse proportion to the energy of the particle. Since this energy is simply dependent on and proportional to the electrical potential through which the charged particle fell before it reached the cathode and not upon its mass, the distribution of intensity along the parabolas will be somewhat similar. There will also be a definite maximum energy corresponding to the whole drop of potential across the discharge tube, with a corresponding minimum displacement on the plate; so that all normal parabolas will end fairly sharply at points p, q, etc., equidistant from the magnetic axis OY. As the ionisation is a maximum in the negative glow the parabolas are brightest at or near these points. The extension of the curves in the other direction indicates the formation of ions at points in the discharge nearer the cathode which will so have fallen through a smaller potential.

19. Secondary Rays.—As the pressure in the camera, though as low as possible, is never entirely negligible, the particles may make collisions, and so gain and lose electrons, while passing through the deflecting fields. This results in what Sir J. J. Thomson calls "secondary rays,"[1] which may be of a great many types. Some appear on the plate as general fog, others as straight beams seeming to radiate from the undeflected spot, these will easily be recognised on the photographs produced in Plate I. Secondary rays can produce parabolas which are very much like the genuine ones caused by particles which have retained their charge through both fields, and which may easily be mistaken for them unless special precautions are taken.

20. Negatively Charged Rays.—As there is intense ionisation in the fine tube the charged particles may easily collide with and capture electrons in passing through it. A

---

[1] J. J. Thomson, *Rays of Positive Electricity*, p. 32.

singly charged particle capturing a single electron will, of course, proceed as a neutral ray, and being unaffected by the fields will strike the screen at the central spot. If, however, it makes a second collision and capture it will become a negatively charged ray. Rays of this kind will suffer deflection in both fields in the opposite direction to the normal ones, and will therefore give rise to parabolas of a similar nature but situated in the opposite quadrants, as indicated by the dotted lines in the figure. Such negative parabolas are always less intense than the corresponding normal ones, and are usually associated with the atoms of electronegative elements such as carbon, oxygen, chlorine, etc.

The negative parabolas of H, C and O can be seen in the photographs. Plate I (1) and (2).

21. Rays with Multiple Charges.—If during ionisation more than one electron is split off, the resulting positive ray will have a double or multiple charge. Taking the case of a doubly charged particle it may give rise to two distinct effects. In the first place, if it retains its double charge while passing through the analysing fields its behaviour will be quite indistinguishable from that of a normal ray of half its mass. Thus the effective mass of the doubly charged oxygen atom, written[1] O^{++}, will be 8. Parabolas due to C^{++} and O^{++} can be seen in Plate I (2). In the second place, the particle may retain its double charge through the whole potential fall of the discharge but capture an electron in the fine tube. It will then constitute a ray of normal ratio of mass to charge but with double the normal energy, so that the normal end of the parabolas will be extended towards the axis OY to a point halfway between that axis and the line *pq*. Such extensions will be seen on the bright parabolas due to carbon and oxygen in the photographs reproduced in Plate I.

Most elements are capable of losing two electrons, some, such as krypton, three or more, while mercury can lose no less than eight at a time. The results of the multiple charge on atoms of mercury is beautifully illustrated in Plate I (3). The parabola *a* corresponding to normal single charge will

---

[1] In the normal singly-charged ray the plus sign is omitted for convenience.

be seen extended almost to the origin itself, while above a series of parabolas of diminishing intensity β, γ, etc., indicate the atoms which have retained two, three or more charges.

22. Dempster's method of positive ray analysis.— It is clear from the considerations on page 27 that if the positive particles all fell through the same potential and so possessed the same energy, a magnetic field alone would suffice to perform their analysis with regard to mass. A method of analysis based on this idea has been devised by Dempster at the Ryerson Physical Laboratory, Chicago.[1]

The method is essentially identical with that used by Classen in his determination of e/m for electrons [2] The charged particles from some source fall through a definite potential difference. A narrow bundle is separated out by a slit and is bent into a semicircle by a strong magnetic field; the rays then pass through a second slit and fall on a plate connected to an electrometer. The potential difference P, magnetic field H, and radius of curvature r determine the ratio of the charge to the mass of the particle by the formula $\frac{e}{m} = \frac{2\mathrm{P}.}{\mathrm{H}^2 r^2}$

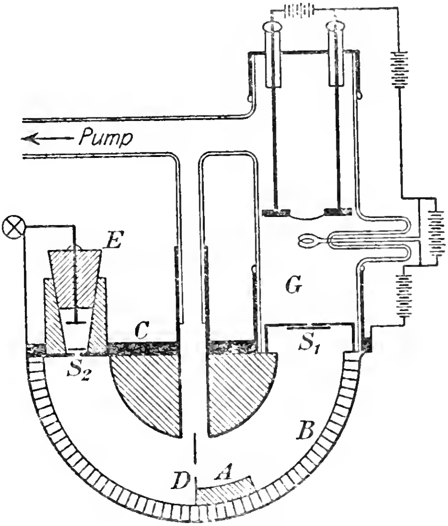


FIG. 5.—Dempster's Apparatus.

---

[1] Dempster, *Phys. Rev.* **11**, 316, 1918.

[2] Classen, *Jahrb. d. Hamburg Wiss. Anst.*, Beiheft, 1907.

The apparatus consisted of a glass tube G, Fig. 5, where the positive particles fell through a definite potential difference, and the analysing chamber A, in which a strong magnetic field was produced between two semicircular iron plates 2·8 cm. thick and 13 cm. in diameter. The iron plates were soldered into half of a heavy brass tube B, so as to leave a passage or slot 4 mm. wide between the plates. A brass plate C closed this slot except for three openings into which short brass tubes were soldered. The glass tube G fitted into the first opening and a tube for exhausting into the second. The electrometer connection passed to a receiving plate through an ebonite plug E which formed a ground conical joint with the third brass tube. The two openings for the rays had adjustable slits S_1, S_2, and a screen D was introduced into the analysing chamber to prevent reflected rays getting into the second slit. The whole was placed between the poles of a powerful electromagnet.

The accelerating potential P was applied by means of a large battery and was from 500 to 1750 volts or thereabouts. The experimental procedure consisted in maintaining a constant magnetic field and plotting the ionic current, measured by the electrometer, against the potential. The peaks on the curve corresponded to definite values of m/e, measured by the potential, and their heights to the relative quantities of the particles present in the beam.

The method is limited in its application by the fact that the ions must be generated with a velocity negligible compared with that produced by the accelerating potential. The first results were obtained from ions produced by heating salts on platinum strips, or by bombarding them with electrons. It was shown that the ions given off from heated aluminium phosphate consisted for the most part of sodium and potassium atoms, and that these had masses 23 and 39 respectively. The resolution possible with the first apparatus was claimed to be about 1 in 100. Dempster's recent successful application of this method to the analysis of magnesium and lithium will be described in a later chapter.[1]

---

[1] *V.* p. 80.

CHAPTER IV

NEON

23. Positive Ray Analysis of Neon.—It is a curious and interesting point that while the first suggestion of the possibility of the occurrence of isotopes was obtained from the rarest of all substances on the earth's surface—the radioactive elements and their products ; so the first result indicating the possibility of isotopes among the stable elements was yielded by neon, a gas of which, in a purified state, there was probably less than one gramme in existence.

Neon is one of the inactive constituents of the atmosphere, in which it occurs to the extent of 0·00123 per cent. by volume. It was first isolated by Ramsay and Travers in 1898, and was accepted as an elementary monatomic element of the helium group. Its density was measured with extreme care by Watson [1] and found to correspond with an atomic weight 20·200 (0 = 16), so that it is the lightest element whose atomic weight differs from a whole number in an unmistakeable manner.

In the summer of 1912 there had been constructed in the Cavendish Laboratory a Positive Ray apparatus which was a considerable improvement on those made previously.[2] The parabolas corresponding to masses differing by 10 per cent. could be clearly resolved and distinguished by its means. Many gases were submitted to analysis ; but no results were obtained which could not be accounted for until in November of that year a sample of the lighter constituents of air was introduced. In describing the results obtained one cannot do

---

[1] Watson, *J.C.S. Trans.* **1,** 810, 1910.

[2] J. J. Thomson, *Rays of Positive Electricity,* p. 20.

better than quote Sir J. J. Thomson's own words from his address to the Royal Institution on Friday, January 17, 1913.

"I now turn to the photograph of the lighter constituents; here we find the lines of helium, of neon (very strong), of argon, and in addition there is a line corresponding to an atomic weight 22, which cannot be identified with the line due to any known gas. I thought at first that this line, since its atomic weight is one-half that of CO_2, must be due to a carbonic acid molecule with a double charge of electricity, and on some of the plates a faint line at 44 could be detected. On passing the gas slowly through tubes immersed in liquid air the line at 44 completely disappeared, while the brightness of the one at 22 was not affected.

"The origin of this line presents many points of interest; there are no known gaseous compounds of any of the recognised elements which have this molecular weight. Again, if we accept Mendeleef's Periodic Law, there is no room for a new element with this atomic weight. The fact that this line is bright in the sample when the neon line is extraordinarily bright, and invisible in the other when the neon is comparatively feeble, suggests that it may possibly be a compound of neon and hydrogen, NeH_2, though no direct evidence of the combination of these inert gases has hitherto been found. I have two photographs of the discharge through helium in which there is a strong line, 6, which could be explained by the compound HeH_2, but, as I have never again been able to get these lines, I do not wish to lay much stress on this point. There is, however, the possibility that we may be interpreting Mendeleef's law too rigidly, and that in the neighbourhood of the atomic weight of neon there may be a group of two or more elements with similar properties, just as in another part of the table we have the group iron, nickel, and cobalt. From the relative intensities of the 22 line and the neon line we may conclude that the quantity of the gas giving the 22 line is only a small fraction of the quantity of neon."

Other samples of gas containing neon all gave similar results. By good fortune some of the purest neon in existence was also available; this had been employed by the writer and Watson in some investigations on the Crookes Dark Space[1] and was actually a part of that by which the atomic weight had been determined. This sample also yielded the two separate parabolas with the same relative intensity as the others. One of the photographs taken with neon is reproduced in Plate 1 (4).

The last result proved that the most careful purification had not appreciably altered the intensity ratio between the lines and might at first sight appear a strong argument for the NeH_2 explanation, but further study of the parabolas only added more weight to the chemical objections against the existence of such a compound. The only other alternative was a novel and revolutionary one, namely that neon could exist in two forms and that the relation between these was precisely that which had been described by Soddy a short time before as existing between the chemically inseparable radio elements.

These considerations led the author to undertake a searching investigation on the constitution of the gas by two distinct lines of attack, first attempts at separation, secondly examination by positive rays.[2]

24. Apparatus for the determination of density.—As neon is chemically inactive the most satisfactory proof of a partial separation of its constituents is a change in density.

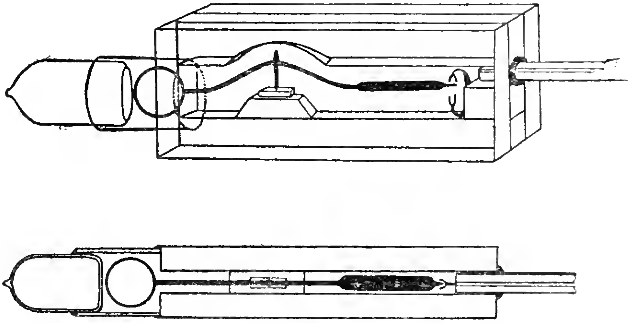


Fig. 6.—Microbalance.

It was therefore necessary to devise some means of determining density accurately, quickly and with the minimum

---

[1] Aston and Watson, *Proc. Roy. Soc.*, **86A**, 1912.

[2] The neon necessary for this research was given by M. Georges Claude of Paris.

quantity of gas. All these desiderata were obtained by the construction of a simple quartz micro-balance shown in Fig. 6.[1]

The principle upon which this works is that if a sealed vacuous quartz bulb is equipoised against a solid piece of quartz on a balance the system can only be exactly balanced, at any predetermined position, when it is immersed in a fluid of an absolutely definite density; if the density is too high the bulb will be buoyed up, if too low it will sink. We can therefore compare the densities of a known and an unknown gas by introducing them successively into the balance case and determining the pressures at which the system is exactly balanced.

The moving part of the balance is made entirely of fused quartz (shown black). It turns upon a single knife-edge cut on a piece of quartz rod about 0·5 mm. thick. To this rod, a few millimetres above the knife-edge, are fused two others about the same thickness forming the arms of the beam. To the end of one arm is fused a sealed vacuous quartz bulb holding about 0·3 c.c. and to the other a counterpoise made of a piece of rod about 2 mm. thick. The beam is supported by its knife-edge on a horizontal quartz plate and housed in a thick glass vacuum-tight case fitting as closely as possible so that its volume is a minimum. The case is connected through the capillary tube shown to a gas pipette and a pump for the introduction and removal of gas and also to a simple form of mercury manometer. The beam was adjusted during its construction so that it balanced in air at about 85 mm. pressure. In the process of adjustment the end of the counterpoise was drawn out into a fine tail ending in a small knob; this was used as the pointer of the beam. The sensitivity of the balance is about 10^{-6} mgrm., which enables the manometer to be set to one-twentieth of a millimetre with ease.

25. Method of using the density balance.—About the right volume of gas, generally known from previous experience, is admitted to the balance case and the mercury level in the manometer slowly raised (increasing the pressure in the balance case) until the bulb rises and the knob at the extremity of the

---

[1] Aston, *Proc. Roy. Soc.*, **89A**, 440, 1914.

counterpoise appears on the field of a fixed reading microscope. The pressure is then carefully adjusted until the knob reaches some definite arbitrary zero point and shows no tendency to move. The pressure is then read off. The gas is now pumped off and the same operation repeated with a gas of known density such as pure oxygen. The ratio of the densities is clearly the inverse of the pressures read, and as the latter are low the molecular weight is given direct without any corrections being required.

Difficulties connected with temperature, so serious in density determinations on the usual scale, are eliminated, for so minute is the quantity of gas (about 0·0005 grm.) used that when this is compressed inside the massive walls of the balance case thermal equilibrium is almost instantaneous. The whole operation of determining the density of a gas to 0·1 per cent. can be completed in ten minutes. Only about half a cubic centimetre of the gas is required for the operation.

26. Experiments on separation by distillation.—The first attempt at separation was made by continual fractionation over charcoal cooled in liquid air. The apparatus used is illustrated in the accompanying figure; the method of working was as follows:—

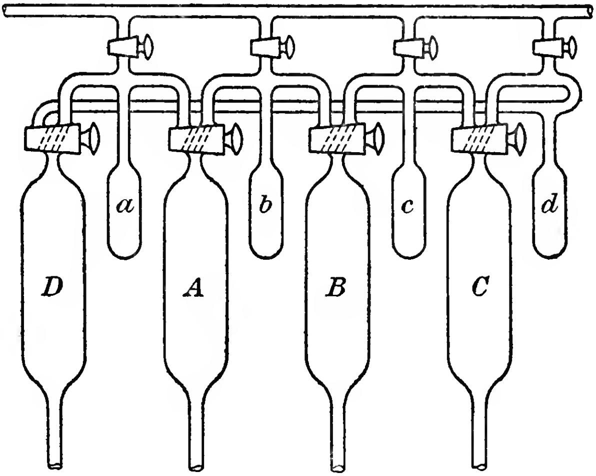


FIG. 7.—Fractionation Apparatus.

The gas was admitted in *a*, one of the small charcoal bulbs *a*, *b*, *c*, *d*, all cooled in liquid air. After a reasonable time had elapsed the first fraction was pumped off by lowering mercury in gas-holder A and opening the connecting stop-cock between it and *a*. After another interval the stopcock was turned, the mercury raised in A and the gas forced into bulb *b*. The mercury was next lowered in both A and B, the former receiving the second fraction from *a* while the latter withdrew the first fraction of the gas now in *b*. The fundamental assumption on which this arrangement was made was that at this stage, if the vapour-pressures of the gases are nearly the same, the gas in A would have the same composition as that left in *b*, and that they therefore might be mixed. This was done by raising the mercury, which not only drove the gas from A into *b* but also the lightest fraction from B into *c*, where it again fractionated, each process driving the lower boiling gas forward and keeping the higher back.

The apparatus may contain any number of units, the whole system being made cyclical and continuous by joining the charcoal bulb at one end with the gas-holder at the other. Four such units were actually employed, and after four operations the liquid air was removed from *a* and the residue it contained was pumped off completely with an Antropoff pump as the first contribution to the heaviest fraction; in the same way that in D was also pumped off as that of the lightest. The bulb *a* was then immersed again in liquid air and the process continued.

After about two-thirds of the gas had been collected in this way as light and heavy fractions, that remaining was all pumped out as the middle fraction. The process was next repeated with the light and heavy fractions in turn, the intermediate ones being combined by a definite rule.

By this arrangement, which does many operations at once, the small quantity of helium contained in the original gas was removed in a remarkably short time, after which the neon was subjected to continual fractionation for three weeks. The gas had now been through about 3000 fractionations and was divided into seven main fractions; the densities of these were determined in order by the quartz micro-balance starting with the lightest, the figures for the pressures giving the same zero as oxygen at 76·35 were as follows:—

(1)	(2)	(3)	(4)	(5)	(6)	(7)
121·05	120·95	121·05	120·90	121·00	121·05	121·05

The mean of these, 121·00, gives a molecular weight of 20·19, which is identical within experimental error with the accepted one of 20·200 determined by Watson. It was evident that no appreciable separation had been achieved.

A positive ray photograph was taken of the two extreme fractions and this showed no appreciable change in the relative intensity of the two parabolas. It was however a very good one for the purpose of measurement and a careful comparison of their displacements with those of the known lines due to CO and CO_2 showed, with a probability almost amounting to certainty, that the atomic weight of the lighter was not as great as 20·20.

Encouraged by this evidence it was decided to make a further attempt at separation by the method of fractional diffusion.

27. Experiments on separation by diffusion.—The first apparatus used was much the same as that described by Ramsay and Collie in their work on the diffusion of argon and helium.[1] The diffusion was carried out at a low pressure and the plug was made of two short lengths of clay pipe in series.

The method of fractionation was that described by Travers.[2] About 100 c.c. of neon was divided first into seven and later into eight fractions. The complete series of fractionations was repeated fifteen times, after which the two extreme fractions were roughly purified over charcoal and their densities measured. These indicated a difference of about a half per cent., a very hopeful result—moreover the lighter fraction showed no appreciable quantity of helium even when analysed by the method of positive rays which is much more delicate than the spectroscope for this purpose.

The extremely laborious process was again taken in hand

---

[1] Ramsay and Collie, *Proc. Roy. Soc.* **60A,** 206, 1896.

[2] Travers, *A Study of Gases*, p. 289.

and the fractionation repeated another twenty-one times, at the end of which the whole of the lightest fraction was lost by a most unfortunate accident. This was the more serious as the two extreme fractions had been systematically enlarged with a view to fractionating each separately.

Despite this setback the fractionation of the heaviest 20 c.c. was proceeded with. This was divided into five fractions and fractionated ten times. The next lightest fraction to the one lost was taken, divided into five parts and fractionated twelve times. These very tedious operations were now brought to a close and the two extreme fractions of 2 to 3 c.c. each were purified over charcoal with the greatest possible care.

The final densities which further purification failed to alter were 20·15 and 20·28 (Oxygen = 32). This change in density is small but it is much too marked to be ascribed to contamination or to experimental error. Looked at in the light of modern knowledge there can be no reasonable doubt that partial separation had been actually achieved. The extent of the separation is about that to be expected from the theoretical considerations of separation by diffusion given on page 127. A spectroscopic examination of these two fractions showed no appreciable difference between them.

These results were announced at the meeting of the British Association at Birmingham in 1913 and at the same time the evidence afforded by the positive ray photographs discussed. This is available from three distinct considerations: the character of the lines, their position and their intensity. A careful examination of the plates showed, when proper allowance had been made for difference of intensity, that the two parabolas had characteristics identical with one another. Both were prolonged towards the vertical axis showing that the particles causing them were equally capable of carrying more than one charge.[1] Now up to that time no cases of multiple charges had been found to occur on molecules, but only on atoms. One was therefore led to infer that both lines were due to elements.

Measurements of the position of the parabolas relative to those of CO and other known bodies in the discharge tube gave

---

[1] *V.* p. 30.

consistent results, indicating that the lighter of the two corresponded with an atomic weight less than 20·2, but the accuracy was not sufficient to make this certain. The relative intensity of the parabolas was estimated by three independent observers as about 10 to 1. Its apparent invariability was valuable corroborative evidence against the possibility of the 22 line being due to the presence of other gases in the discharge tube.

28. Second attempt at separation by diffusion.—In order to carry out further diffusion experiments an elaborate automatic diffusion apparatus was devised so as to avoid the excessive labour of working by hand. This worked on the see-saw principle and dealt with 300 c.c. of neon at a time. It was started in 1914, but as it had little success in its object there is no need to describe it in detail. It will be enough to say that although it performed the mechanical operations of diffusion many thousands of times in a satisfactory manner the separation achieved was exceedingly poor—actually only about half that attained previously. This disappointing result was undoubtedly due to the mistake made in designing it to carry out the diffusion at atmospheric pressure, for under these conditions the "mixing" is very bad.[1]

When the work was interrupted by the war it could be said that although the presence of two isotopes in neon was indicated by several lines of reasoning, none of these could be said to carry absolute conviction.

29. The analysis of neon by the Mass-spectrograph.—By the time the work was resumed in 1919 the existence of isotopes among the products of radioactivity had been put beyond all reasonable doubt by the work on the atomic weight of lead[2] and was accepted generally. This fact automatically increased both the value of the evidence of the complex nature of neon and the urgency of its definite confirmation. It was realised that separation could only be very partial at the best and that the most satisfactory proof would be afforded by measurements of atomic weight by the method of positive rays. These would have to be so accurate as to prove beyond

[1] *V.* p. 127.

[2] *V.* p. 16.

dispute that the accepted atomic weight lay between the real atomic weights of the constituents, but corresponded with neither of them.

A new method of positive ray analysis was therefore worked out which will be described in the next chapter. This proved amply accurate enough for the purpose and the results obtained from neon, which are given in detail on page 64, show beyond any doubt that this gas is a mixture of two isotopes of atomic weights 20·00 and 22·00 respectively.

CHAPTER V

THE MASS-SPECTROGRAPH

30. Limitations of the parabola method.—The parabola method of analysis of positive rays described in Chapter III, though almost ideal for a general survey of masses and velocities, has objections as a method of precision, many rays are lost by collision in the narrow canal-ray tube ; the mean pressure in which must be at least half that in the discharge-bulb ; very fine tubes silt up by disintegration under bombardment ; the total energy available for photography falls off as the fourth power of the diameter of the canal-ray tube.

The first two objections can be overcome, as will be described below, by replacing the brass or copper tube by fine apertures made in aluminium, a metal which appears to suffer little disintegration, and by exhausting the space between these apertures to the highest degree by means of a subsidiary charcoal tube or pump. The falling off in intensity of the parabolas as one attempts to make them finer is a very serious difficulty, as the accuracy and resolving power depend on the ratio of the thickness to the total magnetic deflexion ; and if we increase the latter the electric deflexion must be increased to correspond and the parabolas are drawn out, resulting again in loss of intensity.

Also the nature of the patch thrown on the plate by the use of a long circular tube will clearly be the same as that caused by the light from an evenly illuminated disc passing through a circular aperture of the same diameter, that is to say it will have a penumbra. Similarly the parabolic streak produced by an infinite series of such patches will not be particularly suitable for accurate measurements as it has no definite edges.

31. Methods of increasing the intensity of the spot.—The concentration of the stream of positive rays down the axis of the discharge-bulb is very marked, but there is good evidence for assuming that the intense part of the stream occupies a considerable solid angle. This suggests the possibility of an increase of intensity by means of a device which should select the rays aimed at a particular spot on the plate, whatever direction they come from. For example, a thin gap between two coaxial equiangular cones would allow the rays to be concentrated at the vertex. The dimensions of the patch formed would be roughly those of one given by a cylindrical canal-ray tube of diameter equal to the width of the gap. The increase of intensity would therefore be considerable; but the method is not easy to put into practice, and, in the case of deflexions through large angles, would necessitate a curved photographic surface.

Clearly the simplest way of increasing the intensity of the spot without increasing its dimensions, at any rate in one direction, is to use two parallel straight slits. In the case of the parabola method this device would only be of use in a special case such as the resolution of a close double, as the parabolas will only be sharp at points where they are parallel to the slit.

Such a slit system eliminates the difficulty of the penumbra mentioned above, at any rate so far as measurements at right angles to the line image are concerned.

32. Possibilities of "focussing."—Beams of charged particles which are homogeneous electrically (constant mv^2/e) or magnetically (constant mv/e) can be focussed like rays of light by special devices.[1] The method of Dempster, described in the previous Chapter, makes use of a form of magnetic focussing. But the rays generated by the ordinary discharge bulb are heterogeneous both in mv^2 and mv so that what is required is an arrangement which will focus all rays of constant mass, even though their velocity may vary over an appreciable range.

33. Principle of the Mass-spectrograph.—This purpose

---

[1] Aston, *Phil. Mag.*, **38**, 709, 1919.

is achieved by the arrangement illustrated diagrammatically in Fig. 8. The exact mathematical analysis has now been worked out by R. H. Fowler,[1] but it is proposed to give only the approximate theory here for the sake of simplicity.

The rays after arriving at the cathode face pass through two very narrow parallel slits of special construction S_1 S_2, and the resulting thin ribbon is spread out into an electric spectrum by means of the parallel plates P_1, P_2. After emerging from the electric field the rays may be taken, to a first order of approximation, as radiating from a virtual source *Z* half way through the field on the line S_1 S_2. A group of these rays is now selected by means of the diaphragm D, and allowed to pass between the parallel poles of a magnet. For simplicity the poles are taken as circular, the field between them uniform and of such sign as to bend the rays in the opposite direction to the foregoing electric field.

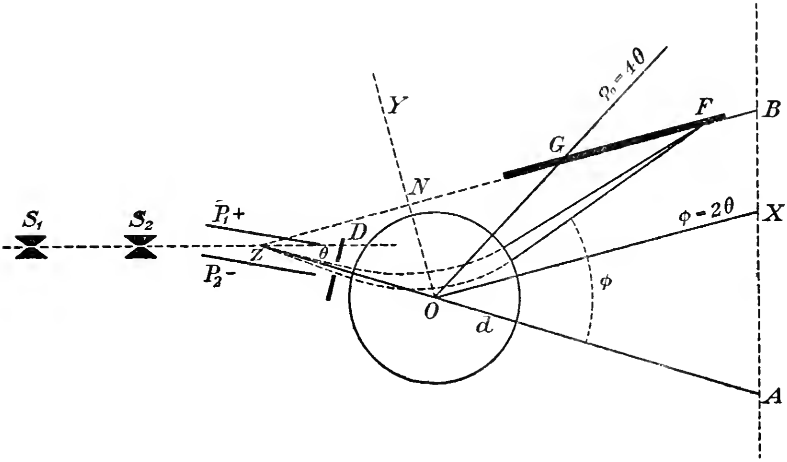


FIG. 8.—Diagram of Mass-Spectograph.

If θ and φ be the angles (taken algebraically) through which the selected beam of rays is bent by passing through fields of strength X and H, then

$$\theta v^2 = lX\frac{e}{m}\ (1), \quad \text{and} \quad \varphi v = LH\frac{e}{m}\ (2),$$

---

[1] Aston and Fowler, *Phil. Mag.*, 1922.

where l, L are the lengths of the paths of the rays in the fields. Equation (1) is only true for small angles, but exact enough for practice. It follows that over the small range of θ selected by the diaphragm θv and φv are constant for all rays of given e/m, therefore

$$\frac{\delta\theta}{\theta} + \frac{2\delta v}{v} = 0, \quad \text{and} \quad \frac{\delta\varphi}{\varphi} + \frac{\delta v}{v} = 0,$$

so that

$$\frac{\delta\theta}{\theta} = \frac{2\delta\varphi}{\varphi},$$

when the velocity varies in a group of rays of given e/m.

In order to illustrate in the simplest possible way how this relation may be used to obtain focussing, let us suppose the angles (exaggerated in the diagram) small and the magnetic field acting as if concentrated at the centre O of the pole-pieces. If the breadth ZO $= b$, the group selected will be spread out to a breadth $b\delta\theta$ at O, and at a further distance r the breadth will be

$$b\delta\theta + r(\delta\theta + \delta\varphi) \text{ or } \delta\theta\left[b + r\left(1 + \frac{\varphi}{2\theta}\right)\right]. \quad . \quad (3)$$

Now as the electric and magnetic deflexions are in opposite directions, θ is a negative angle. Say $\theta = -\theta'$. Then if $\varphi > 2\theta'$, the quantity (3) will vanish at a value of r given by

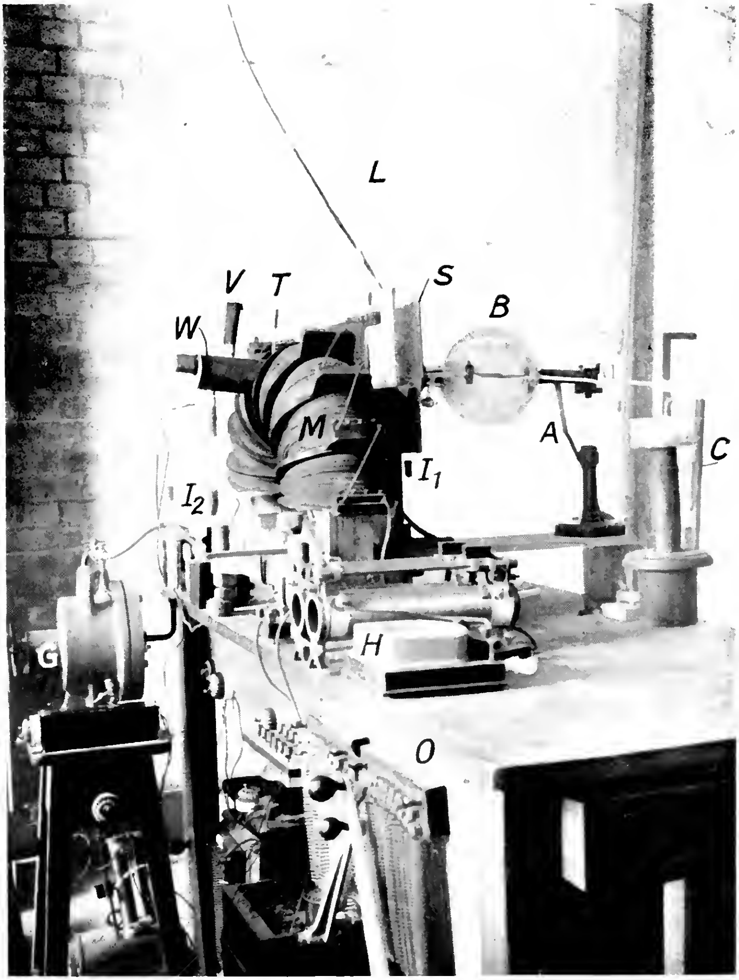
$$r(\varphi - 2\theta') = b \,.\, 2\theta',$$

This equation appears correct within practical limits for large circular pole-pieces.

Referred to axes OX, OY the focus is at $r \cos(\varphi - 2\theta')$, $r \sin(\varphi - 2\theta')$, or r, $b.2\theta'$; so that to a first-order approximation, whatever the fields, so long as the position of the diaphragm is fixed, the foci will all lie on the straight line ZF drawn through Z parallel to OX. For purposes of construction G the image of Z in OY is a convenient reference point, φ being here equal to $4\theta'$. It is clear that a photographic plate, indicated by the thick line, will be in fair focus for values of e/m over a range large enough for accurate comparison of masses.

34. Optical analogue.—It may be a help to form an understanding of the principle of the apparatus if we suppose that the beam is one of white light and the electric and magnetic

PLATE II.



Photograph of the Original Mass-Spectrograph set up in the Cavendish Laboratory in 1919.

B. Discharge Tube. *A*. Anode connected to high potential terminal of induction coil below table. *C*. Reservoir containing gas to be analysed. I_1, I_2. Charcoal-liquid air tubes exhausting slit-system and camera. *S*. Soft iron plates to shield discharge from stray magnetic field. *L*. Leads from high tension battery to electric plates. *M*. Du Bois electromagnet. *T*. Pea lamp for photographing fiducial spot. *V*. Vacuum-tight and light-tight control for moving photographic plate. *W*. Camera showing light-tight cap on the left. *H*. Magnet circuit ammeter. *O*. Magnet circuit control resistances. *G*. Gaede rotating mercury pump connected to the camera and the discharge tube by glass tubes and stopcocks.

fields are glass prisms deflecting the light in opposite directions. The slit system acts as a collimator. If the glass of the first prism has a coefficient of dispersion double that of the second the heterogeneity of the rays of light will cause a spreading of the beam identical with that caused by heterogeneity (in respect to velocity) in the case of the positive rays. It will be clear that if we make the angle of refraction of the second prism more than double that of the first an achromatic image will appear at F.

Since it is a close analogue of the ordinary spectrograph and gives a " spectrum " depending upon mass alone the instrument is called a " mass-spectrograph " and the spectrum it produces a " mass-spectrum." It possesses one notable advantage over the optical spectrograph for, although we can never change the ratio of the dispersions, we can make the refractions whatever we will by the control of X and H, and so bring any desired range of the spectrum on to the plate.

35. The Discharge Tube.—Fig. 9 is a rough diagram of the arrangement of the mass-spectrograph when used for analysing positive rays generated by the ordinary discharge tube method. The discharge-tube B is an ordinary X-ray bulb 20 cm. in diameter. The anode A is of aluminium wire 3 mm. thick surrounded concentrically by an insulated aluminium tube 7 mm. wide to protect the glass walls, as in the Lodge valve.

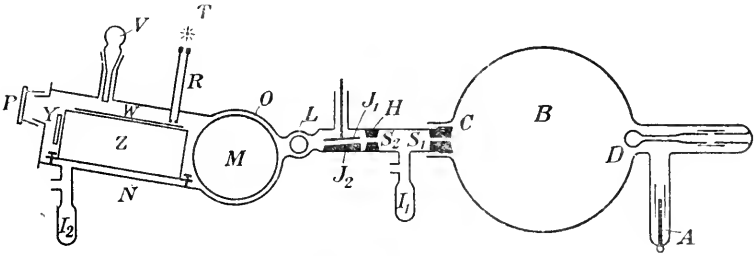


FIG. 9.—Mass-Spectrograph.

The aluminium cathode C, 2·5 cm. wide, is concave, about 8 cm. radius of curvature, and is placed just in the neck of the bulb—this shape and position having been adopted after a short preliminary research.[1] In order to protect the opposite

---

[1] Aston, *Proc. Camb. Phil. Soc.*, **19**, 317. 1919.

end of the bulb, which would be immediately melted by the very concentrated beam of cathode rays, a silica bulb D about 12 mm. diameter is mounted as indicated. The use of silica as an anticathode has the great advantage of cutting down the production of undesirable X-rays to a minimum. The cathode is earthed.

The discharge is maintained by means of a large induction-coil actuated by a mercury coal-gas break; about 100 to 150 watts are passed through the primary, and the bulb is arranged to take from 0·5 to 1 milliampere at potentials ranging from 20,000 to 50,000 volts. Owing to the particular shape and position of the electrodes, especially those of the anode, the bulb acts perfectly as its own rectifier.

The method of mounting the cathode will be readily seen from Fig. 10, which shows part of the apparatus in greater detail. The neck of the bulb is ground off short and cemented with wax to the flat brass collar E, which forms the mouth of an annular space between a wide outer tube F and the inner tube carrying the cathode. The concentric position of the neck is assured by three small ears of brass not shown. The wax joint is kept cool by circulating water through the copper pipe shown in section at G.

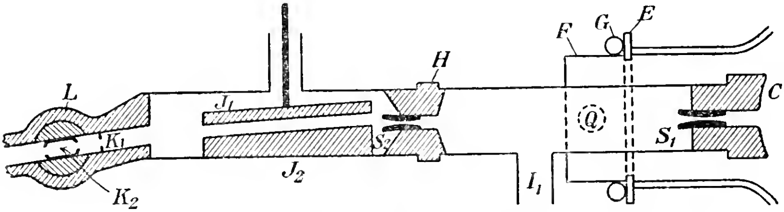


FIG 10.—Mounting of Cathode of Mass-Spectrograph.

The gas to be analysed is admitted from the fine leak into the annular space and so to the discharge by means of the side-tube attached to F shown in dotted section at Q. Exhaustion is performed by a Gaede mercury-pump through a similar tube on the opposite side. The reason for this arrangement is that the space behind the cathode is the only part of the discharge bulb in which the gas is not raised to an extremely high potential. If the inlet or outlet is anywhere in front of the cathode, failing special guards, the discharge is certain to strike to the pump or the gas reservoir. Such special guards have been made in the past by means of dummy cathodes in the bore of the tubes, but, notwithstanding the fact that the gas can only reach the bulb by diffusion, the present arrangement is far more satisfactory and has the additional advantage of enabling the bulb to be dismounted by breaking one joint only.

36. The Slit System.—The very fine slits used in this apparatus were made with comparative ease as follows:—A cylinder of pure aluminium about 10 mm. long by 5 mm. wide is carefully bored with a hole 1 mm. diameter. The resulting thick-walled tube is then cleaned and crushed with a hammer on an anvil until the circular hole becomes a slit about ·3 mm. wide. Continuation of this treatment would result in a slit as fine as required giving the maximum resistance to the passage of gas, but its great depth would make the lining up of a pair a matter of extreme difficulty. The crushed tube is therefore now placed between two V-shaped pieces of steel and further crushed between the points of the V's at about its middle point until the required fineness is attained. Practice shows that the best way of doing this is to crush until the walls just touch, and then to open the slit to the required width by judicious tapping at right angles to that previously employed. With a little care it is possible to make slits with beautifully parallel sides to almost any degree of fineness, ·01 mm. being easily attainable. At this stage the irregularly shaped piece of aluminium is not suited to accurate gas-tight fitting; it is therefore filled with hard paraffin to protect it from small particles of metal, etc., which if entering cannot be dislodged owing to its shape, and turned up taper to fit the standard mountings. After turning, the paraffin is easily removed by heat and solvents. The centre of the cathode is pierced with a 3 mm. hole, the back of which is coned out to fit one of the standard slits S_1. The back of the cathode is turned a gas-tight fit in the brass tube 2 cm. diameter carrying it, the other end of which bears the brass plug H which is also coned and fitted with the second slit S_2. The two slits, which are roughly ·05 mm. wide by 2 mm. long, can be accurately adjusted parallel by means of their diffraction patterns. The space between the slits, which are about 10 cm. apart, is kept exhausted to the highest degree by the charcoal tube I_1. By this arrangement it will be seen that not only is loss of rays by collision and neutralisation reduced to a minimum but any serious leak of gas from the bulb to the camera is eliminated altogether.

37. The Electric Field.—The spreading of the heterogeneous ribbon of rays formed by the slits into an electric spectrum takes place between two parallel flat brass surfaces, J_1, J_2, 5 cm. long, held 2·8 mm. apart by glass distance-pieces, the whole system being wedged immovably in the brass containing-tube in the position shown. The lower surface is cut from a solid cylinder fitting the tube and connected to it and earth. The upper surface is a thick brass plate, which can be raised to the desired potential, 200–500 volts, by means of a set of small storage-cells. In order to have the plates as near together as possible, they are sloped at 1 in 20—i.e. half the angle of slope of the mean ray of the part of the spectrum which is to be selected by the diaphragms. Of these there are two: one, K_1, an oblong aperture in a clean brass plate, is fixed just in front of the second movable one, K_2, which is mounted in the bore of a carefully ground stopcock L. The function of the first diaphragm is to prevent any possibility of charged rays striking the greasy surface of the plug of the stopcock when the latter is in any working position. The variable diaphragm is in effect two square apertures sliding past each other as the plug of the stopcock is turned, the fact that they are not in the same plane being irrelevant. When the stopcock is fully open as sketched in Fig. 10 the angle of rays passing is a maximum, and it may be stopped down to any desired extent by rotation of the plug, becoming zero before any greasy surface is exposed to the rays. Incidentally the stopcock serves another and very convenient use, which is to cut off the camera from the discharge tube, so that the latter need not be filled with air each time the former is opened to change the plate.

38. The Magnetic Field.—After leaving the diaphragms the rays pass between the pole-pieces M of a large Du Bois magnet of 2500 turns. The faces of these are circular, 8 cm. diameter, and held 3 mm. apart by brass distance-pieces. The cylindrical pole-pieces themselves are soldered into a brass tube O, which forms part of the camera N. When the latter is built into position, the pole-pieces are drawn by screwed bolts into the arms of the magnet, and so form a structure of great weight and rigidity and provide an admirable foundation for the whole apparatus. Current for the magnet is provided by a special set of large accumulators. With a potential of 300 volts on the electric plates the hydrogen lines are brought on to the scale at about 0·2 ampere, and an increase to 5 amperes, which gives practical saturation, only just brings the singly-charged mercury lines into view. The discharge is protected from the stray field of the magnet by the usual soft iron plates, not shown.

39. The Camera.—The main body of the camera N is made of stout brass tube 6·4 cm. diameter, shaped to fit on to the transverse tube O containing the pole-pieces. The construction of the plate-holder is indicated by the side view in Fig. 9 and an end-on view in Fig. 11. The rays after being magnetically deflected pass between two vertical earthed brass plates Z, Z about 3 mm. apart, and finally reach the photographic plate through a narrow slot 2 mm. wide, 11·8 cm. long, cut in the horizontal metal plate X, X. The three brass plates forming a **T**-shaped girder are adjusted and locked in position by a set of three levelling-screws, at each end; the right-hand upper one is omitted in Fig. 11. The plates Z, Z serve to protect the rays completely from any stray electric field, even that caused by the photographic plate itself becoming

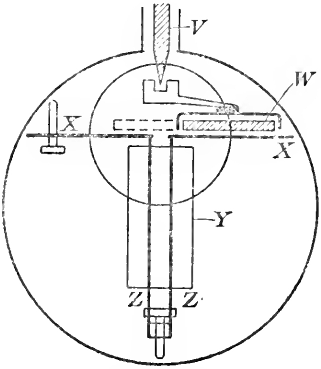


FIG. 11.—The Plateholder of the Camera.

charged until within a few millimetres of their point of impact.

The photographic plate W, which is a 2 cm. strip cut lengthwise from a 5 × 4 plate, is supported at its ends on two narrow transverse rails which raise it just clear of the plate X, X. Normally it lies to the right of the slot as indicated, and to make an exposure it is moved parallel to itself over the slot by means of a sort of double lazy-tongs carrying wire claws which bracket the ends of the plate as shown. This mechanism, which is not shown in detail is operated by means of a torque rod V working through a ground glass joint. Y is a small willemite screen.

The adjustment of the plate-holder so that the sensitised surface should be at the best focal plane was done by taking a series of exposures of the bright hydrogen lines with different magnetic fields on a large plate placed in the empty camera at a small inclination to the vertical. On developing this, the actual track of the rays could be seen and the locus of points of maximum concentration determined. The final adjustment was made by trial and error and was exceedingly tedious, as air had to be admitted and a new plate inserted after each tentative small alteration of the levelling-screws.

40. Experimental procedure.—The plate having been dried in a high vacuum overnight, the whole apparatus is exhausted as completely as possible by the pump with the stopcock L open. I_1 and I_2 are then cut off from the pump by stopcocks and immersed in liquid air for an hour or so. The electric field, which may range from 200 to 500 volts, is then applied and a small current passed through the magnet sufficient to bring the bright hydrogen molecule spot on to the willemite screen Y, where it can be inspected through the plate-glass back of the cap P. In the meantime the leak, pump, and coil, have all been started to get the bulb into the desired state.

When this has become steady, J_1 is earthed to prevent any rays reaching the camera when the plate is moved over the slot to its first position, which is judged by inspection through P with a non-actinic lamp. The magnet current having been set to the particular value desired and the diaphragm adjusted, the coil is momentarily interrupted while J_1 is raised to the desired potential, after which the exposure starts. During this, preferably both at the beginning and the end, light from a lamp T is admitted for a few seconds down the tube R (Fig. 9) the ends of which are pierced with two tiny circular holes. The lower hole is very close to the plate, so that a circular dot or fiducial spot is formed from which the measurements of the lines may be made.

The exposures may range from 20 seconds in the case of hydrogen lines to 30 minutes or more, 15 minutes being usually enough. As soon as it is complete the above procedure is repeated, and the plate moved into the second position. In this way as many as six spectra can be taken on one plate, after which L is shut, I_2 warmed up, and air admitted to the camera. The cap P, which is on a ground joint, can now be removed, and the exposed plate seized and taken out with a special pair of forceps. A fresh plate is now immediately put in, P replaced and the camera again exhausted, in which state it is left till the next operation.

41. Form of the Spectrum Lines.—Owing to the form of the slits used, the shape of the spot formed when undeflected rays from such a slit system strike a photograph surface normally, is somewhat as indicated at *a* (Fig. 12). When they strike the plate obliquely the image would be spread out in one direction, as in *b*. This would be the actual form in the apparatus, if the deflexions of the mean and extreme rays (i.e., the rays forming the centre and the tips) were identical. This is true of the magnetic field since each cuts the same number of lines of force; but it is not so in the case of the electric deflexion. Owing in part to the fact that the plates J_1, J_2 are rectangular and in part to the stray field between the charged plate J_1 and the earthed tube in which it is mounted, the

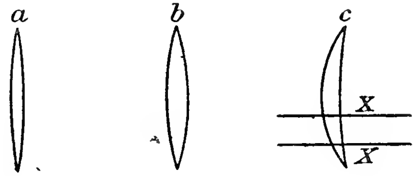


FIG. 12.—Form of the Spectrum Lines.

extreme rays passing diagonally will be deflected more than the mean rays and the spot bent into the form shown at *c*. The convex side will be in the direction of the magnetic deflexion, as this is opposed to the deflexion causing the bend. The image on the plate will therefore be the part of this figure falling on the narrow slot in X, X ; and as the apparatus is not exactly symmetrical, its shape in the spectra is the figure lying between the lines X, X in Fig. 12, *c*.

42. The distribution of the mass-spectrum over the photographic plate.—In order to study the positions of the focus F (Fig 8) on the plate corresponding to different values of the effective mass m when X and H are constant, we may assume perfect focussing and only consider a single median ray. If R is the radius of curvature of the path of a ray of effective mass m while in the magnetic field, and d the radius of the field, clearly $\tan \frac{1}{2} \varphi = d/\mathrm{R}$. But X and θ are constant, hence mv^2 must be constant so that the radius of curvature in the magnetic field varies as $\sqrt{m}$. We may therefore write

$$\tan \tfrac{1}{2} \varphi = \sqrt{(m_0/m)} \quad . \quad . \quad . \quad (4)$$

where m_0 is a constant and can be interpreted as that mass which under the conditions of the experiment is bent through a right angle in the magnetic field.

Again if ON the length of the perpendicular dropped from the centre of the magnetic field upon ZF $= p$ (a constant) then

$$\mathrm{NF} = p \cot (\varphi - 2\theta) \quad . \quad . \quad . \quad (5)$$

By combining (4) and (5) we get an expression for NF/p in terms of m_0 and m. This is complicated,[1] but its differential can be shown to vanish when $\tan \frac{1}{2} \varphi = \tan 2\theta$. Thus the mass-scale is approximately linear near $\varphi = 4\theta$.

This linear law was observed experimentally at the very outset and though at the time it was unexplained it added greatly to the ease and accuracy of the determinations of m.

The quantity actually measured is the distance between a fixed point on the photographic place called the "fiducial spot"[2] and the focussed image F. Let us call this distance D. D and NF differ by a constant k—about 5·4 cm. in the

---

[1] Loc. cit.

[2] *V.* p. 53.

present apparatus—so that the relation between D and m has the form $D = f\ (m/m_0)$ where f is a function in which all the coefficients p, k, and $\tan 2\theta$ are geometrical constants, the fields only affect m_0. It follows directly that so long as the apparatus is rigid:—If D_1 and D_2 are the distances from the fiducial spot of any two points on the plate and m_1 and m_2 the corresponding masses for given values of D_1 and D_2, the ratio m_1/m_2 will be the same in every photograph.

43. Practical method of deducing the effective mass of a particle from the position of its line on the photograph.—The mathematical investigation described above is of interest as it explains the results obtained, but the actual determination of masses from mass-spectra is a purely empirical process, and consists in the comparison of the positions of the lines caused by the masses in question with the positions of known reference lines. The only assumption made was that given at the end of the previous paragraph and even this was capable of verification by experiment, using such methods as that described on p. 57, or even more fundamentally, in the special case of the ratio 2/1, by the known identity of the mass ratios O_2/O, O/O^{++}, and C/C^{++}.

The reference lines used at the outset of the work were lines given by particles of elements and compounds the relative masses of which were known to at least the order of accuracy aimed for. The procedure was somewhat as follows. A series of spectra were taken with say a mixture of CO_2 and CH_4 in the discharge tube. Previous experience with the parabola method of analysis led to the expectation that lines at 6–C^{++}, 8–O^{++}, 12–C, 16–O, 28–CO, 32–O_2, 44–CO_2 would certainly be present, there would also be a series of hydrocarbon lines between 12 and 16, CH, CH_2, CH_3 which could be regarded as known. A spectrum was selected containing as many as possible of these known lines and their masses m_1, m_2, m_3,—were plotted against the distances of the lines from the fixed fiducial spot and a curve drawn through the points so obtained. This is our first *calibration curve*—of necessity inaccurate owing to the gaps between the points. A second spectrum was now taken in which the same lines appeared in a different place, for by altering the magnetic field we can place them wherever we please, and the new set of distances from the fiducial spot measured. These distances were now transformed into masses (no longer integral) m'_1, m'_2, m'_3,—by means of the curve previously drawn. Supposing the curve to be accurate and the ratio law to hold $\frac{m'_1}{m_1} = \frac{m_2}{m_2} = \frac{m'_3}{m_3} = r$ where r is clearly a measure of the change in m_0 in the mathematical discussion above. In practice these ratios were found to be very nearly the same, so that a mean value of r could be taken with confidence. The known masses multiplied by that mean now gave a new set of points on the original curve. By carrying on this process all the serious gaps in the curve could be bridged and its accuracy brought up to the required standard.

The calibration curve so formed renders the identification of one line sufficient to deduce the masses corresponding to all the other lines on the plate, and as in general many lines are known on each spectrum, its accuracy is continually subject to fresh test. In practice it was found perfectly reliable so long as none of the geometrical constants of the apparatus were altered.

Owing to the linear relation at $\varphi = 4\theta$ the actual curve was very nearly straight for a considerable portion of its length. This allowed the following alternative procedure to be adopted if desired. A linear relation was assumed and a table of corrections made by means of reference lines, and these corrections when subtracted from the observed displacements gave an exactly linear relation with mass. A correction-curve (apparently parabolic) was drawn, from which the appropriate correction for any displacement could be written down and the mass corresponding to this displacement obtained by simple proportion.

In connection with the use of reference lines it might be thought difficult to know which of the lines on a plate corresponds to a known mass, since they are not labelled in any way. A little consideration will show that the same difficulty is raised in the case of the standard lines of the iron arc and the stars in the sky, yet neither the spectroscopist nor the astronomer have the least difficulty in recognising enough for their purpose, indeed a mistake in identity would lead in most cases to an error so gross as to compel immediate attention. This comparison is perhaps a little flattering to the lines on a mass-spectrum as these alter their relative intensity to some extent, but in particular cases, such as those of the hydrocarbons and mercury, identification is, after a little experience, as easy as that of the Pole Star or of the D lines in the spectrum of sodium.

44. Comparison of masses by the method of "coincidence."—The method of deducing the masses of particles from the position of their lines described in the foregoing paragraph is simple and straightforward. It also has the great advantage of not requiring an accurate knowledge of the numerical values of the electric and magnetic fields. The only requisite is that these should be constant during the exposure, and even if this constancy is not quite perfect the shift in position will affect all the lines known and unknown alike and therefore introduce no serious error into the results obtained. There is, however, another method of comparing masses which requires no knowledge, either theoretical or empirical, of the relation between effective mass and measured displacement. This is independent of the calibration curve and therefore constitutes a valuable check on results obtained by its use. It depends upon the following considerations:—Suppose we wish to compare an unknown mass m' with a known mass m. A mass-spectrum is taken with fields X and H such that the mass m gives a line at a certain position on the plate. The fields are now altered until the line caused by the unknown mass m' is brought to the identical position on the plate previously occupied by the line due to m. The paths of the rays in the two cases must be identical, hence if X′, H′ are the new values of the fields it follows at once from equations (1) and (2) [1] that $m'/m = \mathrm{X}/\mathrm{X}' \times (\mathrm{H}'/\mathrm{H})^2$. Now it is only necessary to measure one of the fields if we keep the other constant and therefore H, which cannot be measured or reproduced accurately, is kept constant, and X is measured. For the latter purpose it is only necessary to measure the

---

[1] *V.* p. 45.

potentials applied to the plates P_1, P_2, which can be done with the greatest ease and accuracy.

Thus, to take a numerical illustration, the position occupied by the line due to carbon (12) with a potential on the plates of 320 volts should be exactly coincident with that occupied by the line due to Oxygen (16) with 240 volts when the magnetic field is kept constant. All such coincidences have so far been found to occur within the error of experiment, whatever the position on the plate.

Methods depending on the measured variation of X with H constant have some practical disadvantages. The first and most obvious of these is that any small change in the value of the magnetic field between the two exposures will lead to a definite error, this error will be double the percentage change in the field, since the square of the latter is involved. The second objection is founded on considerations of intensity. If the parabola method of analysis is compared with the mass-spectrograph it will readily be observed that, in effect, the latter focusses at a point all the rays which in the former method form a short element of arc on a parabola. The length of the element of arc is determined by the angle of the electric spectrum allowed to pass, i.e. the width of the diaphragm. Its position on the parabola is at our disposal, for, referring to Fig. 4, p. 28, it will be seen that the higher we make X, that is to say the higher the energy of the beam of rays we select at constant θ, the nearer the element of arc will approach the axis OY, in fact its distance from that axis will simply be inversely proportional to X. Also, however many parabolas we consider and however much we move them about by changing H, so long as X is constant the elements of arc selected will all lie on a line parallel to OY. Now it has already been pointed out [1] that the intensity of normal parabolas is a maximum near the head p, where the energy corresponds to the full fall of potential across the discharge tube, and fades away rapidly, in some cases very rapidly indeed, at points more distant from the origin. In order to get the greatest intensity at the focussed spot we must therefore choose X so that the element of arc selected will be near the

---

[1] P. 29.

head of the parabola. This is done in practice by observing visually, by means of a willemite screen, the very bright line given by the hydrogen molecule while different potentials are applied to the plates. The best value of X so determined must also be the best value for all the other normal lines, so that in the ordinary calibration curve method, when X is kept constant, it is possible to use conditions in which all the normal lines on the mass-spectra will be at their brightest together, whatever range we bring on to the plate by altering the magnetic field.

In the coincidence method this very fortunate circumstance cannot be taken advantage of, for with H constant the selected elements of arc will now lie on a line parallel to OX. We can only arrange matters for one, the lighter, of the two masses to be compared, to be at its optimum. In the case of the heavier the selected arc must lie at a greater distance from the origin and therefore provide a much feebler intensity. The disparity in brightness, due to this effect will be the greater the greater the ratio of the masses considered; it can be corrected to some degree by softening the discharge tube while the heavier mass is being photographed.

In spite of these drawbacks the principle underlying the coincidence method is probably the most suitable for mass-ratio measurements of the highest accuracy. The fact that the paths of the rays is the same in the case of both masses eliminates all errors due to non-uniformity of the fields and the results are independent of any assumptions as regards the ratios of the reference lines themselves. It is the only method at present available in the case of elements far removed, on the mass-scale, from the reference lines, and a modification of it called the method of "bracketing" has been successfully used to evaluate the masses of helium and hydrogen.[1]

45. The measurement of the lines.—The accurate determination of the distance of the lines from the fiducial spot is a physical problem of considerable interest. The image itself is due to a caustic of rays, the edge of which will be sharp on the side of maximum magnetic displacement, so

---

[1] *V.* p. 69.

that this, the left side in the Plates, may be expected to maintain its sharpness when a large diaphragm is in use, while the other will fade away gradually. Hence very bright lines will be broadened to the right by this effect (which is analogous to spherical astigmatism in ordinary lenses), but to the left the only broadening will be that due to ordinary halation. The relative importance of these two forms of spreading can be gauged by taking photographs with a very small diaphragm, for then the first will be eliminated and the second can be estimated by comparing lines of different intensity. It is found that for ordinary diaphragm apertures the halation effect is much the smaller ; it can also be minimised by using lines of approximately equal intensity so that the most reliable measurements of lines for position are obtained from their left-hand edges. This is well illustrated in the "bracketed" lines of hydrogen *a* and *c*, Plate III. In (*a*) measurements of the left hand side of the three lines shows this bracket to be really symmetrical though it does not appear so to the eye, on account of the astigmatic spreading of the middle line caused by the use of an open diaphragm and rather too long an exposure. In (*c*) the diaphragm was almost closed and the exposures more carefully adjusted, so that both sides of the lines are sharp and their breadths practically identical.

The most accurate measurements were made on a comparator. The spectrum was set as closely as possible parallel to the axis of the instrument, and the distances between the left-hand edge of the lines and the fiducial spot read off on a Zeiss standard scale. For faint lines it was necessary to use a very low power eyepiece of the reading microscope, and in the case of the faintest lines of all, the best results could be obtained by laying a millimetre scale on the plate and estimating the distance from the fiducial spot to the optical centre of the lines, by the unaided eye.

46. Resolving power and accuracy of mass determination.—Taking the width of the slits as 1/25 mm. and putting in the dimensions of the present apparatus the theory shows that in the region $\varphi = 40$ lines differing by a little less than 1 per cent. should be just separated. In actual practice a better result was obtained, for the instrument is capable of separating the lines of xenon, which differ by 1 in 130; this is probably because the part of the line which falls on the strip of plate exposed is due to the narrower edges of the slits.

The numerical relation between mass and position in this part of the spectrum corresponds to a shift of 1·39 mm. for a change of mass of 1 per cent., so that even with the unaided eye an accuracy of 1 part in 1,000 can be approached. Although it is sufficient in theory to know the mass of one line only to determine, with the calibration curve, the masses of all the others, in practice every effort is made to bracket any unknown line by reference lines and only to trust comparative measurements when the lines are fairly close together. Under these conditions an accuracy of 1 in 1,000 is claimed and there is little doubt that in favourable cases it is exceeded.

47. Order of results and nomenclature.—In the descriptions of the results obtained with the mass-spectrograph contained in the following chapters the order of the elements given is, when possible, that in which the experiments were made. There is a practical reason for this procedure, as in most cases it was impossible to eliminate any element used before the following one was introduced. Evacuation and washing have little effect, as the gases appear to get embedded in the surface of the discharge bulb and are only released very gradually by subsequent discharge.

The problem of nomenclature of the isotopes became serious when the very complex nature of the heavy elements was apparent. It has been decided for the present to adopt the rather clumsy but definite and elastic one of using the chemical symbol of the complex element, with an index corresponding to its mass: e.g. Ne^{22}, Rb^{87}. This system is made reasonable by the fact that the constituents of complex elements have all so far proved to have masses expressible in whole numbers.

48. Lines of the First, Second and higher Orders.—It was shown on page 30 that particles having two charges gave a parabola corresponding to an effective mass of one half the normal mass. In the same way a particle with three charges will have an effective mass of one third, and so on.

These apparent masses will duly make their appearance on mass-spectra as lines corresponding to simple fractions of the real mass causing them. It is convenient in these cases to borrow the nomenclature of optics and refer to the lines given by singly, doubly, and multiply charged particles respectively as lines of the first, second, and higher orders. Thus the molecule of oxygen gives a first order line at 32, and its atom first and second order lines at 16 and 8.

The empirical rule that molecules only give first order lines [1] is very useful in helping to differentiate between atoms and compound molecules of the same apparent mass. Some results given below,[2] however, show that in certain cases it breaks down, so that inferences made from it must not be taken as absolutely conclusive.

49. Negative mass-spectra.—It has been mentioned that positive rays could become negatively charged by the capture of electrons by collisions in the narrow canal-ray tube of the Thomson apparatus, and so produce parabolas in the quadrant opposite to that containing the normal ones. The slit system of the mass-spectrograph is specially designed to eliminate such collisions as far as possible by exhausting the space between the slits. If the means of exhaustion of this space is deliberately cut off, and the normal electric and magnetic fields both reversed in sign it is possible, at a small cost in definition of the lines, to photograph the mass-spectra of negatively charged particles. Such negatively charged particles are only formed by elements or compounds having marked electronegative properties. Very little work has been done in this interesting field, but certain ambiguities in the interpretation of the chlorine results have been satisfactorily cleared up by its means.

---

[1] J. J. Thomson, *Rays of Positive Electricity*, p. 54.

[2] *V.* p. 75.

CHAPTER VI

ANALYSIS OF THE ELEMENTS

50. Arrangement of results.—In this Chapter and the one following it are given the experimental results obtained from a large number of elements which have been subjected to analysis with a view to determining their constitution. This Chapter deals with those elements which, by reason of their volatility or properties of forming volatile compounds, can be treated by the ordinary discharge-tube method. The analysis given in all these cases is that obtained by means of the mass-spectrograph.

In Chapter VII will be found the results obtained by the analysis of those elements, all metals, whose positive rays must be generated by special devices. Here the analyses are effected by several different methods.

The sequence of the elements in the two Chapters is that in which the results were obtained; with the exception of nickel, which is included in the first group although its mass-spectrum was not obtained until after the other metals had been under observation.

51. Oxygen (At. Wt. 16·00) and Carbon (At. Wt. 12·00).—On a mass-spectrum all measurements are relative, and so any known element could be taken as a standard. Oxygen is naturally selected. Its molecule, singly-charged atom, and doubly-charged atom give reference lines at 32, 16, and 8 respectively. The extremely exact integral relation between the atomic weights of oxygen and carbon is itself strong evidence that both are "simple" elements, and so far no evidence appears to have arisen to throw any doubt on this point. Direct comparison of the C line (12) and the CO line (28) with the above standards shows that the whole number relation and additive law hold to the limit of accuracy, i.e. one part in a thousand; and this provides standards C^{++} (6) C (12), CO (28), and CO_2 (44).

Many of these lines will be recognised on the spectra reproduced on Plate III. The compounds of carbon and hydrogen provide two valuable and easily distinguishable groups of reference lines. The first, which may be called the C_1 group, contains five:—12-C, 13-CH, 14-CH_2, 15-CH_3, 16-CH_4 (or O). It is very well shown on Spectrum V, Plate III. When water vapour is present, and particularly when a fresh discharge-tube is used for the first time, it is followed by 17-OH, 18-OH_2, and sometimes by 19 presumably OH_3 but always very faint. The second hydrocarbon or C_2 group contains seven lines:—24, 25, 26, 27, 28, 29, 30, which include the very strong and particularly valuable reference line 28 CO or C_2H_4. This group is well illustrated in Spectra I and II, Plate III. All the above lines may be expected on spectra obtained by the ordinary discharge-tube method; for an addition of CO or CO_2 is usually made to the gases or vapours under consideration and assists the smooth running of the discharge. The hydrocarbons are derived from the wax and grease used in the joints of the apparatus.

52. Neon (At. Wt. 20·20).—As soon as the instrument was found to work satisfactorily and enough mass-spectra containing reference lines had been obtained, neon was introduced into the discharge tube. The best results were obtained with a mixture of carbon monoxide and neon, containing about 20 per cent. of the latter gas.

The two first order and two second order lines due to neon were all four available and well placed for measurement on the mass spectra obtained. The following figures are taken from the original paper;[1] they are the results of the measurements made on two different plates, using six different spectra.

PLATE 1.

First order.		*Second order.*	
20·00	22·00	9·98	11·00
19·95	22·01	10·02	10·99
19·97(5)	22·00(5)	10·00	10·99(5)

---

[1] Aston, *Phil. Mag.*, **39**, 454, 1920.

PLATE 2.

20·00	21·90	10·01	11·06
19·98	22·10	9·98	10·98
20·00	22·03	9·98	11·01
19·90	21·98	—	—
19·97	22·00(5)	9·99	11·01

The method of measuring the position of the lines then in use, combined with a photographic halation effect,[1] tended to decrease the masses given by very bright lines. This is enough to account for the reading of the intense 20 line giving a mass a little too low. The above figures therefore can be accepted as conclusive evidence that neon is a mixture of two isotopes of atomic weights 20·00 and 22·00 (O = 16) respectively, to an accuracy of about one-tenth per cent.[2]

The two first order lines of neon are shown in Spectrum I, Plate III, but, of course, their relative intensities must not be judged from such a half-tone reproduction. On the original negatives the intensities are in good agreement with the expected ratio 9 to 1 which is necessary to yield the accepted atomic weight 20·20.

53. Possibility of a third isotope of neon.—On some of the clearest spectra obtained with neon present there is a distinct indication of a line corresponding to a mass 21. This is an exceedingly faint line and, at first, was thought to indicate the presence of a third isotope. It is now considered more probably due to an abnormal hydride of the kind discussed on page 98.

54. Chlorine (At. Wt. 35·46).—Spectra indicating that this element was a mixture of isotopes were first obtained by the use of hydrochloric acid gas, but as this was objectionable on account of its action on mercury, phosgene ($COCl_2$) was substituted. Spectra II, III, and IV, Plate III, are reproduced from one of the plates taken with this gas. Spectrum I is reproduced for comparison, it shows the state of the tube before chlorine compounds were introduced. It will be seen

---

[1] *V.* p. 60.

[2] Aston, *Nature*, Nov. 27, 1919; *Phil. Mag.* **39**, 454, 1920.

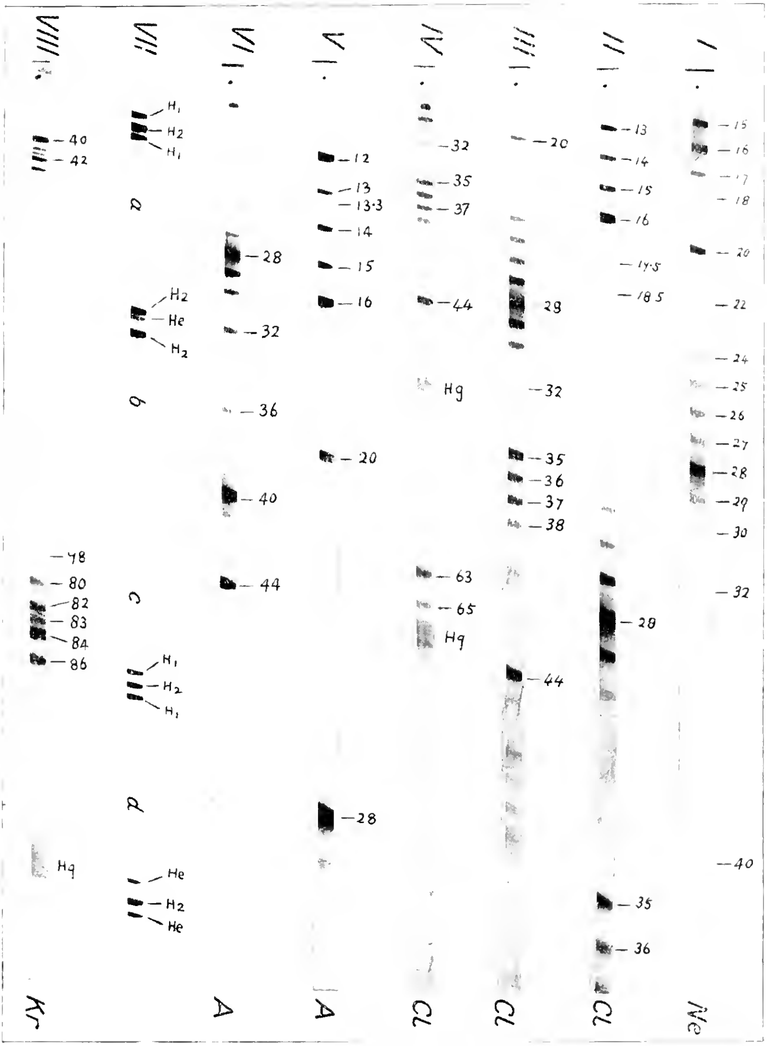
that chlorine is characterised by the appearance of four very definite lines in the previously unoccupied space to the right of O_2 (32): measurement shows these lines to correspond exactly to masses 35, 36, 37, and 38. On Spectrum II, Plate III, taken with a small magnetic field, faint lines will be seen at 17·5 and 18·5. These only appeared when chlorine was introduced, and are certainly second order lines corresponding to 35 and 37. Chlorine is therefore a mixture of isotopes, and two of these have masses 35 and 37. Evidence that Cl^{35} and Cl^{37} are the main if not the only constituents is given by the strong lines 63 and 65 (Spectrum IV, Plate III), due to $COCl^{35}$ and $COCl^{37}$. The lines 36 and 38 were naturally ascribed to the hydrochloric acids corresponding to Cl^{35} and Cl^{37}.[1] That this surmise is correct was definitely proved about a year later when the mass spectra of negatively charged rays of chlorine were successfully obtained in the manner described on p. 62. On the negative mass spectra produced in this way only the two chlorine lines 35 and 37 could be distinguished. The property of forming negatively charged ions is a purely chemical characteristic; that isotopes of the same element should differ radically in it is quite out of the question. It is therefore perfectly certain that the lines 36 and 38 are not, to any sensible extent, due to isotopes of chlorine.

On many of the spectra obtained from chlorine compounds a very faint line is distinguishable at 39. This was regarded as a possible third isotope (which would then be an isobare of potassium. No decision on this point has been obtained from the negative mass spectra, for these have, so far, been too faint for the 39 line to be visible, even if it was present. A careful comparison between the intensity of this line and those at 35 and 37 on a large number of plates discloses an apparent variation which tells rather decidedly against the idea that a third isotope is present. More evidence, however, will be necessary to clear this point.

55. Argon (At. Wt. 39·88 Ramsay, 39·91 Leduc).—The tube was run with a mixture of CO_2 and CH_4, and then about 20 per cent. of argon added. The main constituent of the

---

[1] Aston, *Nature*, Dec. 18, 1919; *Phil. Mag.*, **39,** 611, 1920.



Mass Spectra.

(By kind permission of the Editors of The Philosophical Magazine.)

element was at once evident from a very strong line at 40 (Spectrum VI, Plate III), reproduced in the second and third orders at 20 and 13·33 (Spectrum V). The third order line is exceedingly well placed for measurement, and from it the mass of the singly-charged atom is found to be 40·00 ± ·02. At first this was thought to be the only constituent, but later a faint companion was seen at 36, which further spectra showed to bear a very definite intensity relation to the 40 line. No evidence drawn from multiple charges was available in this case owing to the probable presence of OH_2 and C; but the above intensity relation and the absence of the line from spectra taken just before argon was introduced, made it extremely likely that it was a true isotope.

Any doubt on this point has been removed for all practical purposes by results obtained during the later work on krypton and xenon. Argon was always present to more or less extent during these experiments and the invariable association of a line at 36, of appropriate intensity, with the stronger one at 40 may be regarded as confirming the original conclusion in a satisfactory manner. The presence of 3 per cent. of this lighter isotope is sufficient to reduce the mean atomic weight from 40 to 39·9.

56. Nitrogen (**At. Wt. 14·01**).—This element shows no abnormal characteristics: its atom cannot be distinguished, on the present apparatus, from CH_2 nor its molecule from CO. Its second order line on careful measurement appears to be exactly 7, so it is evidently a simple element, as its chemical combining weight would lead one to expect.

57. Hydrogen (**At. Wt. 1·008**) **and Helium** (**At. Wt. 3·99**).—In connection with the analysis of positive rays the element hydrogen is of peculiar interest in many ways. Its invariable presence in rays generated by the ordinary discharge-tube method, no matter what gas is being employed, is itself a very striking phenomenon, even when due allowance has been made for its abnormal power in affecting screens and plates.

The ease with which its brilliant lines, the molecular one in particular, can be generated and observed visually is of an importance hardly to be exaggerated in the development and technique of the mass-spectrograph. The advantage of the visible presence of the H_2 line has already been referred to [1] and was realised very keenly in the investigation of the alkali metals when the method precluded the use of this line to indicate when suitable conditions for exposure had been obtained.[2]

The hydrogen atom is the lightest particle ever observed to carry a positive charge, which agrees very well with the generally accepted idea that the true Moseley number of this element is 1. This implies that the neutral atom of hydrogen only contains one electron and therefore can only acquire a single positive charge in losing it. The singly charged particle so formed is therefore *the "proton" or ultimate atom of positive electricity itself.*

Helium, on the other hand, can lose two electrons and acquire a double charge, indeed its atoms are invariably in this state when ejected from the nuclei of radioactive elements as alpha rays. Nevertheless, in spite of every effort to obtain the second order line of helium—for direct comparison with the hydrogen molecule—not the faintest indication of it has yet been observed on a mass spectrum, although there is not the least difficulty in obtaining its first order line to any intensity required.

The explanation of this is probably to be found in the very high ionisation potential—about 80 volts [3]—associated with the detachment of both electrons. If doubly charged helium atoms are formed in the discharge tube—and we have every reason to consider this probable—their chance of passing through the slit system and the deflecting fields without picking up a single electron may be practically nil. This is made the more likely by the fact that helium is not absorbed by charcoal and liquid air, so that when it is present the pressure in the apparatus tends to become undesirably high.

---

[1] *V.* p. 52.

[2] *V.* p. 87.

[3] Franck and Knipping, *Phys. Zeit.*, **20,** 481, 1919; *Ver. Deut. Phys. Ges.* **20,** 181, 1919; and Horton and Davies, *Proc. Roy. Soc.* **95A,** 408, 1919; *Phil. Mag.* **39,** 592, 1920.

58. The determination of the masses of atoms of hydrogen and helium by the method of "Bracketing."[1]—The determination of masses so far removed as these from the ordinary reference lines offers peculiar difficulties, but, as the lines were expected to approximate to the terms of the geometrical progression 1, 2, 4, 8, etc., the higher terms of which are known, a special method was adopted by which a two to one relation could be tested with some exactness. Two sets of accumulators were selected, each giving very nearly the same potential of about 250 volts. The potentials were then made exactly equal by means of a subsidiary cell and a current-divider, the equality being tested to well within 1 in 1000 by means of a null instrument. If exposures are made with such potentials applied to the electric plates first in parallel and then in series, the magnetic field being kept constant, all masses having an exact two to one relation will be brought into coincidence on the plate.[2] Such coincidences cannot be detected on the same spectrum photographically; but if we first add and then subtract a small potential from one of the large potentials, two lines will be obtained which closely bracket the third. To take an actual instance—using a gas containing hydrogen and helium, with a constant current in the magnet of 0·2 ampere, three exposures were made with electric fields of 250, 500 + 12, and 500 — 12 volts respectively. The hydrogen molecule line was found symmetrically bracketed by a pair of atomic lines (Plate III, Spectrum VII, *a* and *c*), showing within experimental error that the mass of the molecule is exactly double the mass of the atom. When after a suitable increase of the magnetic field the same procedure was applied to the helium line and that of the hydrogen molecule, the bracket was no longer symmetrical (Spectrum VII, *b*), nor was it when the hydrogen molecule was bracketed by two helium lines (*d*). Both results show in an unmistakable manner that the mass of He is less than twice that of H_2. In the same way He was compared with O^{++}, and H_3.[3] The method is discussed on p. 57. The values obtained by its use can be checked in the ordinary way by

---

[1] Aston, *Phil. Mag.* **39,** 621, 1920.

[2] *V.* p. 57.

[3] *V.* p. 70.

comparing He with C^{++} and H_3 with He, these pairs being close enough together for the purpose. The following table gives the range of values obtained from the most reliable plates :—

Line.	Method.	Mass assumed.	Mass deduced.
He	Bracket	$O^{++} = 8$	3·994–3·996
	Direct	$C^{++} = 6$	4·005–4·010
H_3. . . .	Bracket	$C^{++} = 6$	3·025–3·027
	Direct	He $= 4$	3·021–3·030
H_2. . . .	Bracket	He $= 4$	2·012–2·018

From these figures it is safe to conclude that hydrogen is a simple element and that its atomic weight, determined with such consistency and accuracy by chemical methods, is the true mass of its atom.

This result leads to theoretical consideration of the greatest importance, which will be discussed later.[1]

59. Triatomic Hydrogen H_3.—The occurrence of a parabola corresponding to a mass 3 was first observed and investigated by Sir J. J. Thomson.[2] He came to the conclusion that it was probably due to triatomic hydrogen. The simplest way of obtaining this substance is to bombard KOH with cathode rays and pump off the gases so produced. The H_3 used for the above measurements was obtained in this way. The mass deduced proves in a conclusive manner that the particle causing it is a molecule of three hydrogen atoms, a result independently established about the same time by the chemical work of Wendt and Landauer.[3]

60. Krypton (At. Wt. 82·92) and Xenon (At. Wt. 130·2).—The results with these elements were particularly interesting. The first source available, was the remains of two small samples of gas from evaporated liquid air. Both contained nitrogen, oxygen, argon, and krypton, but xenon was only detected spectroscopically in one and its percentage in that must have been quite minute. Krypton is characterised by a remarkable

[1] *V.* p. 100.

[2] J. J. Thomson, *Rays of Positive Electricity*, p. 116, 1913.

[3] Wendt and Landauer, *Jour. Am. Chem. Soc.* **42**, 930, 1920.

group of five strong lines at 80, 82, 83, 84, 86, and a faint sixth at 78. This cluster of isotopes is beautifully reproduced with the same relative values of intensity in the second, and fainter still in the third order. These multiply-charged clusters give most reliable values of mass, as the second order can be compared with A (40) and the third with CO or N_2 (28) with the highest accuracy. It will be noted that one member of each group is obliterated by the reference line, but not the same one. The singly and doubly charged krypton clusters can be seen to the right and left of Spectrum VIII, Plate III. It will be noticed that krypton is the first element examined which shows unmistakable isotopes differing by one unit only.

On the krypton plates taken with the greatest magnetic field faint, but unmistakable indications of lines in the region of 130 could just be detected. The richest sample was therefore fractionated over liquid air, and the last fraction, a few cubic millimetres, was just sufficient to produce the xenon lines in an unmistakable manner. Five could be distinguished, but owing to difficulties in the way of accurate measurement the provisional values first published were one unit too low.

Later on in March, 1921, a sample of gas was obtained which contained a large proportion of xenon, though it was by no means free from krypton. This yielded some excellent mass spectra, which not only served to correct the figures given for the five isotopes discovered previously, but also indicated the possibility of two additional ones.

The absolute position of the group on the mass scale was satisfactorily fixed by means of the second order line of the strongest member, which fortunately lies outside the third order mercury group. This gave constant and accurate values corresponding to 64·5. The five strong lines of xenon are therefore 129, 131, 132, 134, 136. On the left of the first there was to be seen on many of the plates distinct indications of a faint component 128. Also the darkening between the lines 129 and 131 appears decidedly greater than that to be expected from ordinary halation and suggests the possibility of a seventh isotope 130. The relative intensity of the lines of krypton and xenon is best indicated in Fig 17, p. 109.

61. Mercury (At. Wt. 200·6).—As this element is employed both in the apparatus for the admission of gas and in the Gaede vacuum pump, it would be very difficult to eliminate it entirely from the discharge. This is fortunately neither necessary nor desirable in most cases, for it provides a valuable reference scale and, for some reason unknown, its presence is definitely beneficial to the smooth running of the discharge tube.

Mercury is abnormal in its capacity for forming multiply-charged particles. A study of its remarkable parabolas[1] enabled Sir J. J. Thompson to show that the atom of mercury can carry no less than eight charges, that is lose eight electrons. He gives reasons for considering that it loses all eight at once and then recaptures them one at a time, so giving rise to a series of parabolas 200/1, 200/2, 200/3, etc. The brightest is the first, which is due to atoms which have recaptured all but one electron; the others are progressively fainter.

Subjected to the greater resolving power of the mass spectrograph it was seen at once that mercury was a complex element. Its first, second, third, and higher order lines appeared as a series of characteristic groups around positions corresponding to masses 200, 100, $66\frac{2}{3}$, etc. Some of these will be easily distinguished on the spectra reproduced. The second, third and fourth order groups are well shown in Spectrum VIII, Plate IV. Careful study of the group shows that it consists of a strong line 202, a weak one 204 and a strong group 197–200 which cannot be resolved on the present instrument, but which in all probability contains all the four integers in that range.

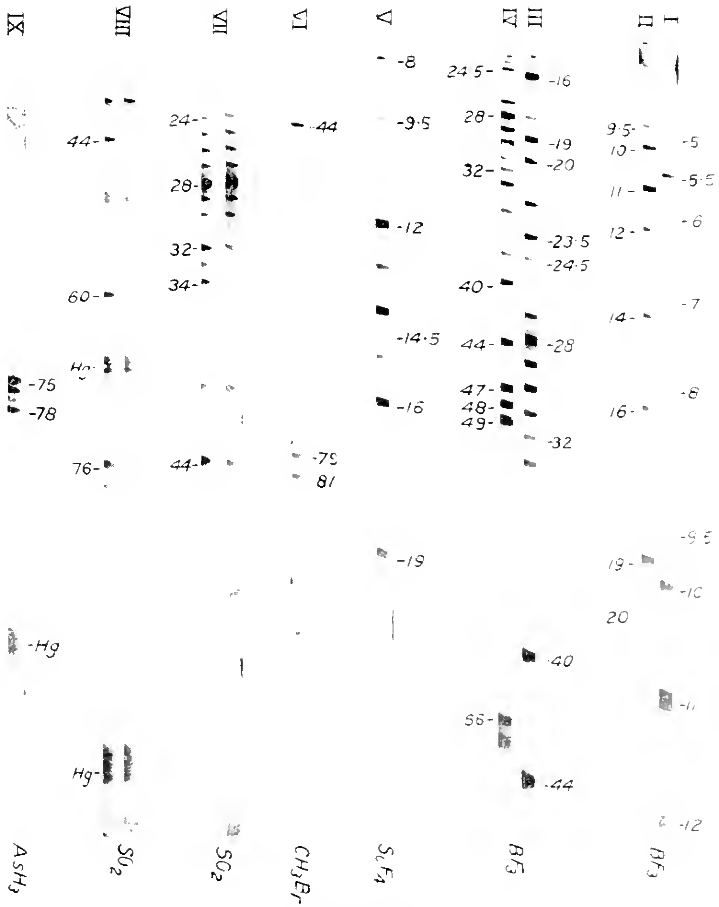
62. Boron (At. W. 10·90). Fluorine (At. W. 19·00). Silicon (At. W. 28·3).—It will be convenient to treat of these three elements together. The atomic weights of boron and fluorine have both been recently redetermined by Smith and Van Haagen[2] with the above results. On the atomic weight of silicon there is some divergence of opinion. The

---

[1] *V.* Plate I (3).

[2] Smith and Van Haagen, *Carnegie Inst. Washington Publ.* No. 267, 1918.

PLATE IV.



Mass Spectra.

(By kind permission of the Editors of The Philosophical Magazine.)

international value is quoted above, but Baxter, Weatherell, and Holmes make it nearer 28·1.[1]

After a failure to obtain the boron lines with some very impure boron hydride, a sample of boron trifluoride was prepared from boric acid and potassium borofluoride, and this gave good results. Following the usual practice, it was mixed with a considerable quantity of CO_2 before introduction into the discharge-tube. Very complex and interesting spectra were at once obtained, and it was remarked that this gas possessed an extraordinary power of resurrecting the spectra of gases previously used in the apparatus. Thus the characteristic, first and second order lines of krypton were plainly visible, although the tube had been washed out and run many times since that gas had been used. This property of liberating gases which have been driven into the surface of the discharge-bulb is doubtless due to the chemical action of the fluorine, liberated during the discharge, on the silica anticathode and the glass walls. After running some time the corrosion of the anticathode was indeed quite visible as a white frost over the hottest part.

After several successful series of spectra had been secured, the percentage of boron trifluoride in the gas admitted was increased as far as possible, until the discharge became quite unmanageable and the tube ceased to work. Just before it did, however, it yielded two very valuable spectra which confirmed the isotopic nature of boron. These are reproduced side by side as they were taken (Spectra I & II) Plate IV. The lines at 10 and 11 are undoubtedly both first-order lines of boron. The hypothesis that these might be due to neon liberated by the action mentioned is not tenable, both on account of their relative intensities and the absence of *strong* neon first-order lines. Even if it were, it could not explain the presence of the well-defined lines at 5 and 5·5 which had never been obtained before at all, and which must be second-order lines of boron. This element therefore has at least two isotopes 10 and 11. The relative photographic intensity of

---

[1] Baxter, Weatherell and Holmes, *Journ. Am. Chem. Soc.*, **42**, 1194, 1920.

the lines 5 and 5·5 does not agree well with an atomic weight as high as 10·9, and the discrepancy might be explained by the presence of a third isotope at 12; which would be masked by carbon, for it has not yet been found practicable to eliminate carbon from the discharge. But Plate IV, Spectrum IV, contradicts this suggestion for, as will be shown later, the line at 49 is mainly if not wholly due to $B^{11}F_2$, so that there should also be a line at 50 for $B^{12}F_2$. The line at 49 is very strong, but at 50 any small effect there may be can safely be ascribed to the fourth order of mercury. The evidence is clearly against the presence of a third isotope of boron.

The exceedingly accurate whole-number value for the atomic weight of fluorine suggests the probability of this element being simple. This conclusion is borne out by the strong line at 19·00 with second-order line at 9·50. The accompanying line at 20, very faint in Spectrum II, Plate IV, is no doubt HF. As there is no evidence whatever to the contrary, fluorine is taken to be a simple element with an atomic weight 19.

Having adopted these values for boron and fluorine, we may now apply them to Spectra III and IV, Plate IV, taken with boron trifluoride. Consider first the group of three very strong lines 47, 48, and 49. The last two are to be expected as being due to $B^{10}F_2$ and $B^{11}F_2$ respectively, but since there is no evidence of a boron 9 or a fluorine 18, line 47 cannot be due to a compound of these elements. But line 47 only appeared when BF_3 was introduced, and so must be due to silicon fluoride formed by the action of the fluorine on the glass walls and the silica anticathode.

To test this the BF_3 was washed out and replaced by SiF_4, which had been made by the action of sulphuric acid on calcium fluoride and silica in the usual way. This greatly reduced the lines 48 and 49, and so they must be attributed to boron compounds. At the same time line 47 remained very strong, and was evidently due to a compound $Si^{28}F$, so that silicon has a predominant constituent 28. This conclusion is further supported by the presence of very strong lines at 66, $Si^{28}F_2$ and 85, $Si^{28}F_3$.

The chemical atomic weight shows that this cannot be its only constituent. Lines at 29, 48, 67, and 86 all suggest a silicon of atomic weight 29. Practically conclusive proof of this is given in Spectrum V, Plate IV, which shows its second-order line unmistakably at 14·50. The only other reasonable origin of this line, namely second-order $B^{10}F$, is eliminated by the fact that there is no trace of a line at 10 in this spectrum.

The evidence of a silicon of atomic weight 30 is of a much more doubtful character. Its presence is suggested by the lines 30, 49, 68, and 87, but the possibility of hydrogen compounds makes this evidence somewhat untrustworthy, and no proof can be drawn from a second-order line 15, as this is normally present and is due to CH_3. On the other hand, if we accept a mean atomic weight as high as 28·3, the relative intensity of the lines due to compounds of Si^{28} and Si^{29} indicates the probable presence of an isotope of higher mass. These considerations taken with the complete absence of any definite evidence to the contrary make the possibility of Si^{30} worth taking into account.

63. Molecular lines of the Second Order.—The work of Sir J. J. Thomson on multiply-charged positive rays showed very definitely that molecules carrying more than one charge were at least exceedingly rare,[1] for not a single case was observed which could not be explained on other grounds. Up to the time of the experiments with the fluorine compounds the same could be said of the results with the mass-spectrograph. This absence of multiply-charged molecular lines, though there is no particular theoretical reason for it, has been used as confirmatory evidence on the elementary nature of doubtful lines.

The spectra obtained with BF_3 show lines for which there appears no possibility of explanation except that of doubly-charged compound molecules. The two most obvious of these may be seen on Plate IV, Spectrum III, and at the extreme left-hand end of Spectrum IV. They correspond to masses 23·50 and 24·50, the first being quite a strong line. Were there no lines of lower order corresponding to these, the whole-number rule might be in question; but all doubt is removed

---

[1] J. J. Thomson, *Rays of Positive Electricity*, p. 54.

by the fact that the lines 47 and 49 are two of the strongest on the plate. A comparison of several spectra upon which these lines occur shows a definite intensity relation which practically confirms the conclusion that the first pair of lines are true second-order lines corresponding to the first order lines of the second pair. Now lines 47 and 49 cannot by any reasonable argument be elementary, they must in fact be due to compounds of fluorine with boron $B^{11}F_2$ or silicon $Si^{28}F$, or due to both. Further evidence of the capability of fluorine compounds to carry two charges is offered by line 33·50, which is undoubtedly the second-order line corresponding to 67, i.e. $B^{10}F_3$ or $Si^{29}F_2$. So far as results go, fluorine appears to be unique in its power of yielding doubly-charged molecules in sufficient number to produce second-order lines of considerable strength.

64. Bromine (At. Wt. 79·92).—The results with this element were definite and easy to interpret. Its chemical combining weight is known with great certainty, and is very nearly the whole number 80. It was rather a surprise, therefore, that it should give a mass-spectrum which showed it to consist of a mixture of two isotopes in practically equal proportions. Methyl bromide was used for the experiments, and one of the results is reproduced in Plate IV, Spectrum VI. The characteristic group consists of four lines at 79, 80, 81, and 82. 79 and 81, apparently of equal intensity, are much the stronger pair, and are obviously due to elementary bromines. This result is practically confirmed by second-order lines at 39·5 and 40·5 too faint to reproduce, but easily seen and measured on the original negative. The fainter pair, 80 and 82, are the expected lines of the two corresponding hydrobromic acids.

65. Sulphur (At. Wt. 32·06).—Spectra VII and VIII, Plate IV, show the effect of the addition of sulphur dioxide to the gas in the discharge-tube. Above each is a comparison spectrum taken immediately before the gas was admitted, on the same plate with approximately the same fields. The very marked strengthening of lines 32 and 44 is no doubt due to S and CS. New lines appear at 33 SH, 34 SH_2, 60 COS, 64 SO_2

or S_2, and 76 CS_2. It may be noticed that lines 32, 60 and 76 are accompanied by a faint line one unit higher and a rather stronger line two units higher. In the first case it is certain and in the others probable that these are, at least partly, due to hydrogen addition compounds. If a higher isotope of sulphur exists, as is suggested by the chemical atomic weight, it seems unlikely that this should have mass 33, for this would have to be present to the amount of 6 per cent., and should give a line at 35 one-thirteenth the strength of 34 (normal SH_2). No such line is visible. A sulphur of atomic weight 34 present to the extent of 3 per cent. is more likely, but there is hardly enough evidence as yet to warrant its serious consideration.

66. Phosphorus (At. Wt. 31·04). Arsenic (At. Wt. 74·96).—The gases phosphine PH_3 and arsine AsH_3 were used in the experiments on these elements, and the results were of notable similarity. The mass-spectrum of each gas was characterised by a group of four lines. The first and strongest doubtless due to the element itself, the second rather weaker due to the monohydride, the third very faint to the dihydride, and the fourth fairly strong to the trihydride. The spectrum of AsH_3 is shown in Spectrum IX, Plate IV; that of phosphorus is similar but its lines are weak, and therefore unsuited to reproduction. Both elements appear to have no isotopes, and neither give visible second-order lines.

67. Selenium (At. Wt. 79·2). Tellurium (At. Wt. 127·5).—The compounds used in the experiments on these elements were selenium hydride, made by passing a stream of hydrogen through boiling selenium, and tellurium methyl. Complete failure resulted in both cases. There was, indeed, on one spectrum an exceedingly faint line at 79, but no shred of reliable evidence could be found to ascribe it to an isotope of Se. In the case of tellurium no trace of any line near 127 could be discovered. The failure is unfortunate in the case of Te on account of its well-known anomalous position in the periodic table; in the case of Se particularly so for the following reasons:—If the accepted atomic weight is even approximately correct this element must have one isotope, at least, of atomic weight greater than 78. But the numbers 79, 80, 81, 82, 83, 84, are already filled by isotopes of Br and Kr, so that it is extremely probable that one of the isotopes of Se has an atomic weight identical with one of an element having a different atomic number, i.e. is an Isobare. The latter are known to exist among radioactive elements, but none have so far been discovered during the work on mass spectra.

68. Iodine (At. Wt. 126·92).—The results with this element were fortunately both definite and conclusive. Methyl iodide was employed, its vapour being introduced mixed with CO_2 and CH_4. It gave one strong line at 127 satisfactorily confirmed by another single line at 142 due to CH_3I.

This proves iodine to be a simple element in an unequivocal manner, a rather unexpected result since all the speculative theories of element evolution, by Van den Broek and others, predict a complex iodine.

69. Antimony (At. Wt. 120·2).—Antimony hydride SbH_3 was used. This was made by dissolving antimony magnesium alloy in dilute acid. Unlike the corresponding arsenic compound it gave an entirely negative result, no line whatever being distinguishable in the region expected from the atomic weight. This failure is probably to be ascribed to the exceedingly unstable nature of the antimony compound.

70. Tin (At. Wt. 118·7).—Tin tetrachloride was employed in the investigation of this element. The vapour of this compound attacks the tap grease used in the apparatus, which makes it extremely difficult to deal with. The results were entirely negative except in one case. On this occasion a second attempt to get the selenium line from selenium hydride was actually in progress, but a good deal of $SnCl_4$ vapour had been introduced previously, and the chlorine lines were so intense that some "resurrected" compound of chlorine must have been the principal factor in the discharge. For some unknown reason the discharge tube was working abnormally well. On one of the spectra then obtained, Spectrum II, a group of lines of *even* integral mass 116, 118, 120, 122, 124 (followed by iodine 127) could be distinguished and some of these may possibly have been due to isotopes of tin. This supposition is slightly strengthened by the appearance of a still fainter group of *odd* integral mass containing the lines 155, 157, etc., which might be isotopic tin monochlorides. It has not been found possible to repeat this result, so that no reliance is to be put upon it.

71. Nickel (At. Wt. 58·68).—Nickel received attention early in the history of positive rays as it is one of the elements whose atomic weight is out of order in the periodic table; it should be heavier, not lighter than cobalt (58·97). It is amenable to treatment in the ordinary discharge tube for it forms an easily vaporisable carbonyl compound $Ni(CO)_4$. Unfortunately this is very rapidly decomposed by the electric discharge, so that in the early experiments made by Sir J. J. Thomson the walls of the discharge bulb became coated with a black deposit of the metal, it was impossible to maintain a steady discharge for a sufficient time, and no satisfactory parabola corresponding to the element could be obtained.

Quite recently [1] by the use of abnormally high current intensities in the discharge it has been found possible to overcome these difficulties to some extent and to obtain a satisfactory mass spectrum from a mixture of nickel carbonyl and carbon dioxide. This consists of two lines, the stronger at 58 and the weaker at 60. They are most conveniently placed between the mercury groups of the third and fourth order, with which they can be compared with an accuracy of one-tenth per cent. The results were also checked by comparison with the CO_2 line at 44, and appear to be integral within the above error. Nickel therefore consists of at least two isotopes. The intensities of the lines are about in the ratio 2 : 1, and this agrees with the accepted atomic weight. It may be noticed that had the heavier isotope preponderated the atomic weight of the element would have appeared normally placed in the periodic table.

---

[1] *Nature*, June 23, 1921, p. 520.

CHAPTER VII

ANALYSIS OF THE ELEMENTS (*Continued*)

72. Positive Rays of Metallic Elements.—Positive rays of most of the metallic elements cannot be obtained by the ordinary discharge-tube method, since in general they have extremely low vapour-pressures and are incapable of forming stable volatile compounds. Mercury is a notable exception to this rule, and its rays are exceedingly easy to produce.

Positively charged rays which appeared to be atoms of the alkali metals were first observed by Gehrcke and Reichenheim.[1] They obtained them by two distinct methods: the first, which may be conveniently called the "*Hot Anode*" method, consisted in using as anode of the discharge-tube a platinum strip coated with a salt of the metal and electrically heated by an external battery. The second device, with which they performed most of their pioneer work on Anode Rays, was to use a *composite anode* of special construction which worked without the need of external heating.

73. Dempster's analysis of Magnesium (At. Wt. 24·32).—The experiments of Dempster with the "hot anode" method of generating positive rays have already been noted.[2] Later,[3] he announced the very important discovery of the three isotopes of magnesium, and subsequently published an account of the experimental details.[4] The magnesium rays were obtained from a piece of the metal which was heated electrically by a coil of wire, and at the same time bombarded by electrons from a Wehnelt cathode. The occluded gases

---

[1] Gehrcke and Reichenheim, *Ver. d. Phys. Gesell.*, **8,** 559, 1906; **9,** 76, 200, 376, 1907; **10,** 217, 1908.

[2] P. 31. [3] Dempster, *Science*, Dec. 10, 1920.

[4] Dempster, *Proc. Nat. Ac. Sci.*, **7,** 45, 1921.

were first driven off, and then the heating current was increased till the metal was slightly vaporised and the magnesium lines appeared. The following description of the analysis and the curves obtained are taken direct from Dempster's paper :—

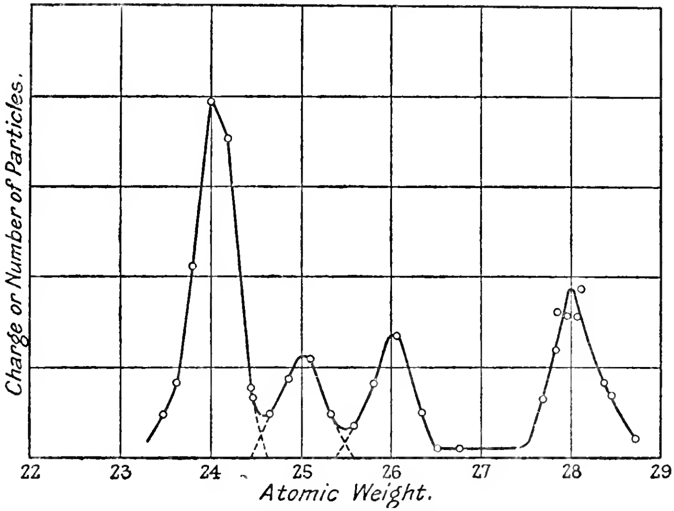


Fig. 13.—Curve for Magnesium.

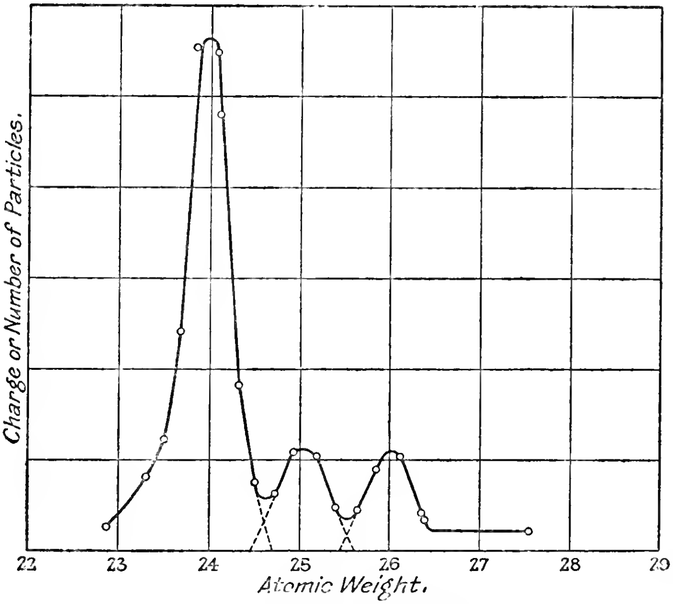


Fig. 14.—Curve for Magnesium.

"The charged atoms of different atomic weights are successively brought on to the detecting electrode by keeping the magnetic field constant and varying the potential which accelerates the rays, the potential required being inversely proportional to the mass of the particles. Thus, if one atomic weight is known the others may be found. Due to the finite width of the slits, each element gives a curve, on the atomic weight scale, which is theoretically a linear increase to a maximum and then a linear decrease. The width half way to the maximum is given by $m. \frac{2S}{d}$ where m is the atomic weight, S the slit width and d the diameter of the circle in which the rays travel. Under good vacuum conditions this theoretical sharpness is practically obtained. For 1 mm. slits this width of the curves should thus be one-half a unit on the atomic weight scale. The former measurement with the apparatus and the magnetic field determinations sufficed to locate elements between 20 and 30 within one unit, and identified the strong nitrogen rays (possible carbon monoxide) of molecular weight 28 which are given off when the metal is first heated.

"One series of experiments was as follows. After heating the magnesium slightly and pumping, till a MacLeod gauge gave no pressure indication, the nitrogen molecule was the only particle present. The heating current was then increased by steps to vaporise the magnesium. With 0·7 ampere, 28 alone was present, with 0·75 ampere an arc apparently struck as the cathode-anode current jumped suddenly to five times its value. The electron current was decreased to its former value by cooling the cathode and the rays were measured. It was found that three strong new lines had appeared. The new lines which are undoubtedly due to magnesium were compared with the nitrogen rays which were still faintly present and found to have atomic weights, 24, 25 and 26. The observations are illustrated in Fig. 13, which gives the current or number of particles for different atomic weights. The nitrogen line had its maximum at 817 volts, and the atomic weight abscissae are 28 × 817 divided by the volts applied. The ordinates of the 28 line are multiplied by 10 in plotting to make them comparable with the other three lines. The dotted continuation to the axis indicates the slight overlapping of the lines. We conclude that magnesium consists of three isotopes of atomic weights 24, 25 and 26.

"Later curves made with steadier discharge conditions are more suitable than Fig. 13 for measuring the relative strengths of the components. In Fig. 13 there appears to have been a drop in intensity just before 24 was reached, in the measurement from high to low atomic weights. The curve is of interest as still containing 28 faintly and so serving accurately to locate the weights which otherwise would have been uncertain to a fraction of a unit.

"Fig. 14 is one of several later curves taken under steadier conditions. These all have very closely the same appearance. The components 25 and 26 are present very nearly in equal amounts; in some measurements 25 was found about nine-tenths the intensity of 26. The component at 24 is approximately 6 times as strong as the one at 26. The ratio of 1 : 1 : 6 gives an average atomic weight 24·375, which is in as good agreement with the accepted atomic weight for magnesium as could be expected with the wide slits used in these first experiments."

74. The mass-spectra of the alkali metals.—In order to analyse the metals of this group a modification of Gehrcke and Reichenheim's hot anode method was employed by the writer to generate the positive rays. After a certain amount of initial difficulty in technique had been overcome this gave satisfactory results.[1]

The apparatus for producing the rays was very simple, and will be readily understood from the figure (Fig. 15). The hot anode A is a strip of platinum foil ·03 mm. thick, about 2 mm. wide by 7 mm. long, welded to the two stout platinum leads which are fused through the glass at C. It was raised to the required temperature by current from one large storage-cell connected through a rheostat as shown. As the anode is of necessity the high-potential pole of a discharge-tube arranged to give positive rays, this heating arrangement had to be very carefully insulated. The anode was mounted on a ground

---

[1] Aston, *Phil. Mag.*, **42**, 436, 1921.

joint as indicated so that it could be easily removed and replaced. The discharge-tube was cylindrical, about 4 cm. in diameter, mounted concentric to the axis of the perforated cathode K. A side tube was fitted at B which could be cooled in liquid air ; in some of the experiments this was charged with charcoal.

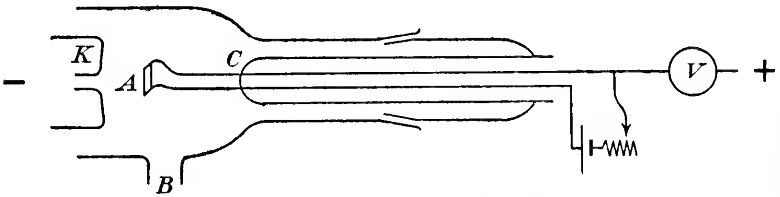


FIG. 15.—Hot Anode Discharge Tube.

The anode was placed immediately opposite the perforation of the cathode and about 1 cm. away from it. The platinum strip was bent at one end into a U-shaped channel into which the salts could be melted. The discharge was maintained by a large induction-coil used in the previous work on mass spectra and rectified by means of a valve V.

75. Experiments with the Parabola method of analysis.—In the preliminary experiments the analysis of the rays was performed by Sir J. J. Thomson's " parabola " method, since this gives the maximum general information, and it was only when suitable conditions and technique had been ascertained that the mass spectrograph was applied.

The general procedure was to pump out the discharge-tube to the lowest possible pressure, far lower than that necessary to prevent all discharge with the anode cold, and then to heat up the anode until the discharge started. This usually happened at dull red heat, and by very careful adjustment of the temperature and of the primary current in the coil it was possible, under favourable conditions, to maintain a fairly steady current of 1 to 2 milliamperes at a potential of about 20,000 volts.

It will be seen that the arrangement resembles that of a Coolidge X-ray tube reversed pole for pole, and it was hoped that it might share the outstanding controllability of that device ; but that expectation was only very partially realised.

The mechanism of the discharge is extremely obscure, for the current intensity is, of course, enormously in excess of that to be expected from the ordinary thermionic release of positive ions from the hot anode.[1] There was very little visible glow in the tube, the X-radiation was small and, although a faint cloud of sodium light nearly always appeared in front of the red-hot anode, the pressure was too low for the anode rays to be visible ; their point of impact with the cathode could, however, be inferred from the scintillations on its surface.

Observations of this effect lead to the conjecture that the bulk of the rays originate not from the surface of the salt itself but from that of the heated platinum, and also that some points on this are much more active than others, giving rise to jets of rays. The direction of these jets seemed to depend on the local configuration of the strip and was beyond practical control. The obvious device of moving the anode about by means of the ground joint to get a radiant point in the required place could not be applied, for the parabolas were never bright enough to be visible on the willemite screen. To add to these difficulties the salt disappeared very rapidly, in some cases in a few minutes. Consequently exposures were very limited in duration, and even in the most favourable cases the results rarely had a satisfactory intensity.

The preliminary experiments were done with sodium phosphate, and before long encouraging results were obtained. In all the successful exposures only a single parabola appeared, and this showed that—although the method on account of the number of inevitable failures is an exasperating one to use—as a means of identifying isotopes it has the great merit of producing the positive rays of the metals and *no others.* This characteristic seems to be due to the very low pressure employed and also possibly to the position of the anode itself, which prevents any positive rays generated in more distant parts of the tube from ever reaching the perforation in the cathode in the necessary axial direction.

Such a selective action has two very important results. In the first place, it eliminates the many ambiguities of the

---

[1] Richardson, *The Emission of Electricity from Hot Bodies*, p. 234 et seq., Longmans, 1916.

ordinary mass spectrum due to multiply-charged rays, or to hydrogen and other addition products ; but, in the second, it prevents the use of the oxygen line as a comparison standard. As soon as it was demonstrated beyond any reasonable doubt that sodium was a simple element (and its chemical atomic weight is so exactly integral on the oxygen scale as to be conclusive corroboration) it was taken as standard at 23.

76. Lithium (At. Wt. 6·94).—The most successful experiment done with the parabola method of analysis was one in which a mixture of sodium and lithium phosphates was employed (this contained traces of potassium salts). By great good fortune a very strong jet of rays must have been directed along the axis and three satisfactory exposures were obtained before the anode dried up. One of these is reproduced in Plate I (5) A strong parabola at 7 and a weak one at 6 demonstrate clearly that lithium is a complex element, as its chemical atomic weight 6·94 leads one to expect. This result, which was announced by the writer and G. P. Thomson in *Nature*, February 24th, was confirmed independently by Dempster [1] using the method described for magnesium. The several photographs here considered all gave approximately the same ratio of intensities, and they corresponded as well as was to be expected with the accepted atomic weight. On the other hand, G. P. Thomson's parabolas (which were obtained with a composite anode) and Dempster's electrical measurements suggest a more nearly equal intensity ratio and this ratio appears to vary.

77. Sodium (At. Wt. 23·00).—Sodium gave the brightest effects, and its single line was obtained so intense that the presence of another constituent to the extent of even less than 1 per cent. could probably have been detected. It may therefore be safely regarded as a simple element.

The parabola method of analysis is perfectly satisfactory in the case of so light an element as lithium, but cannot be used for the critical examination of the heavier members of the group ; and so the apparatus for the production of the

---

[1] Dempster, *Science*, April 15, 1921.

rays was fitted to the mass spectrograph already described.[1] The experimental difficulties became now very serious indeed, for, in addition to those already indicated, there was no means of finding the most suitable voltage to apply to the electrostatic plates. In normal cases this is done by visual inspection of the hydrogen lines, but here it could only be guessed at. Under these conditions it is not a matter for surprise that the photographs, though sufficient for the purpose of detecting isotopes, only gave very faint lines and so cannot be reproduced as illustrations.

78. Potassium (At. Wt. 39·10).—A mixture of potassium sulphate, potassium bromide, and a little sodium phosphate was now used on the anode, and after several unsuccessful attempts some fairly satisfactory spectra were obtained which contained both sodium and potassium lines. Using the former as standard the latter consisted of a bright component at 39, and a very faint component at 41.

79. Rubidium (At. Wt. 85·45).—Rubidium chloride was now added to a little of the mixture used in the potassium experiments and spectra containing the potassium and rubidium lines were obtained. Rubidium is very definitely double. Its components are more nearly equal in intensity than those of lithium or potassium. Measured against the potassium line 39 its stronger component is 85 and the weaker 87. The intensity ratio agrees reasonably well with the accepted atomic weight 85·45.

80. Caesium (At. Wt. 132·81).—When a mixture of rubidium chloride and caesium chloride was used evidence of a line at 133, measured against the two rubidium lines, was soon obtained. Pure caesium chloride was then substituted and the utmost possible exposure given to search for a lighter component, which was to be expected from the fractional chemical atomic weight 132·81. Although by this means the intensity of the line 133 was increased to a satisfactory pitch no other neighbouring line was found. If, therefore, a lighter isotope of caesium exists it must differ from 133 by many

---

[1] *V.* Chap. V.

units—which seems very unlikely—or it cannot be present in proportion sufficient to account for the fractional atomic weight obtained by chemical means.

81. Thompson's work on Beryllium (At. Wt. 9·1).—G. P. Thomson [1] has recently investigated the Anode rays obtained from a composite anode similar to that devised by Gehrcke and Reichenheim [2] and has subjected them to analysis by the parabola method. After the parabolas of the isotopes of lithium had been successfully obtained [3] he went on to investigate the element beryllium. The best results were obtained from a mixture of sodium bromide and beryllium fluoride. This gave a single strong parabola corresponding to an atomic weight 9 (Na = 23). The accepted chemical atomic weight is rather higher, so a careful examination was made to discern any possible faint companions at 10 or 11. He concludes that neither of these can be present to any sensible extent, and therefore that beryllium is probably a simple element.

82. Calcium (At. Wt. 40·07) and Strontium (At. Wt. 87·63).—Thomson also obtained by the same method parabolas due to these elements, the latter very faint, but the resolution at his disposal was too low to decide their constitution. From the position of the strong parabola of calcium he concludes that one or more of the atomic weights 39, 40, 41 were present ; and as all these are already known to exist as isotopes of either potassium or argon, it follows that calcium must be an isobare of one or other of these elements.[4]

83. Table of Elements and Isotopes.—The following list tabulates the results contained in this and the previous Chapter. The isotopes of complex elements are given in the order of the proportions present. Brackets indicate that the figures are provisional only.

---

[1] G. P. Thomson, *Phil. Mag.*, **42**, 857, 1921.

[2] *V.* p. 80.

[3] *V.* p. 86.

[4] *V.* p. 148.

Table of Elements and Isotopes

Element.	Atomic number.	Atomic weight.	Minimum number of isotopes.	Masses of isotopes in order of intensity.
H . .	1	1·008	1	1·008
He . .	2	4·00	1	4
Li . .	3	6·94	2	7, 6
Be . .	4	9·1	1	9
B . .	5	10·9	2	11, 10
C . .	6	12·00	1	12
N . .	7	14·01	1	14
O . .	8	16·00	1	16
F . .	9	19·00	1	19
Ne . .	10	20·20	2	20, 22, (21)
Na . .	11	23·00	1	23
Mg . .	12	24·32	3	24, 25, 26
Si . .	14	28·3	2	28, 29, (30)
P . .	15	31·04	1	31
S. . .	16	32·06	1	32
Cl . .	17	35·46	2	35, 37, (39)
A . .	18	39·88	2	40, 36
K . .	19	39·10	2	39, 41
Ni . .	28	58·68	2	58, 60
As . .	33	74·96	1	75
Br . .	35	79·92	2	79, 81
Kr . .	36	82·92	6	84, 86, 82, 83, 80, 78
Rb . .	37	85·45	2	85, 87
I . .	53	126·92	1	127
X . .	54	130·2	5, (7)	129, 132, 131, 134, 136, (128, 130 ?)
Cs . .	55	132·81	1	133
Hg . .	80	200·6	(6)	(197–200), 202, 204

Dempster's later results (*V. p.* 148)

Ca . .	20	40·07	(2)	(40, 44 ?)
Zn . .	30	65·37	(4)	(64, 66, 68, 70)

CHAPTER VIII

THE ELECTRICAL THEORY OF MATTER

84. The Whole Number rule.—By far the most important result of the measurements detailed in the foregoing chapters is that, with the exception of hydrogen, the weights of the atoms of all the elements measured, and therefore almost certainly of all elements, are whole numbers to the accuracy of experiment, in most cases about one part in a thousand. Of course, the error expressed in fractions of a unit increases with the weight measured, but with the lighter elements the divergence from the whole number rule is extremely small.

This enables the most sweeping simplifications to be made in our ideas of mass, and removes the only serious objection to a unitary theory of matter.

85. The Unitary Theory of the constitution of matter.—From the very earliest times it has been a favourite hypothesis that all matter is really composed of one primordial substance, Air, Fire, Earth and Water have all been suggested in the past.

The first definite theory of the constitution of the atoms of the elements out of atoms of a primordial element (Protyle, Urstoff, etc.) was made by Prout in 1815. *Prout's Hypothesis* was that the atoms of the elements were different aggregations of atoms of *hydrogen*. On this view it is obvious that the atomic weights should all be expressed by whole numbers when the atomic weight of hydrogen itself is taken as unity. Owing to the roughness of the methods available and the considerable inaccuracies of the atomic weight determinations made at that time there was little to disprove the hypothesis, and its marked simplicity gained it many adherents. But as time went on chemical methods grew more precise and it became more and more impossible to reconcile experimental results with integral combining weights until the evidence against it was strong enough to cause J. S. Stas (1860–1865) to state: "I have arrived at the absolute conviction, the complete certainty, so far as it is possible for a human being to attain to certainty in such matters, that the law of Prout is nothing but an illusion, a mere speculation definitely contradicted by experience."

Nevertheless, though abandoned temporarily by the chemist as impracticable, the idea of primordial atoms appealed strongly to the mind of the philosopher and the physicist. Herbert Spencer, in his hypothesis of the constitution of matter, says: "All material substances are divisible into so-called elementary substances composed of molecular particles of the same nature as themselves; but these molecular particles are complicated structures consisting of congregations of truly elementary atoms, identical in nature and differing only in position, arrangement, motion, etc, and the molecules or chemical atoms are produced from the true or physical atoms by processes of evolution under conditions which chemistry has not been able to reproduce."

The discovery of the electron, the proof that it was the same whatever the atom from which it was detached and, most important of all, the demonstration by Sir J. J. Thomson and others that electricity could simulate the known properties of matter, gave us the key to the riddle of what these primordial atoms really are. The only serious obstacle, the fractional atomic weights, has now been removed so that there is nothing to prevent us accepting the simple and fundamental conclusion:—The atoms of the elements are aggregations of atoms of positive and negative electricity.

86. The Atom of Negative Electricity, or Electron.—

The fundamental unit of negative electricity makes its appearance in physical phenomena in many guises, such as the cathode ray of electrical discharge, the beta ray of radioactive change, the thermion of the wireless valve. A very complete account of it has recently been published by Millikan[1] so that it is not proposed to describe its history and properties at any length

---

[1] *The Electron*, by R. A. Millikan, University of Chicago Press, 1917.

here. It will be sufficient to note a few of its more important constants.

Its charge e is given by Millikan as $4{\cdot}774 \times 10^{-10}$ E.S.U. The most reliable measurements of e/m for the electron, at low velocity, give the value $5{\cdot}30 \times 10^{17}$ E.S.U. Hence its mass is almost exactly $9{\cdot}00 \times 10^{-28}$ grs., 1845 times less than the mass of the hydrogen atom, or 0·00054 on the ordinary scale of atomic weights (Oxygen = 16).

87. The atom of Positive Electricity, or Proton.—Our physical knowledge of this body is not nearly so complete as that of its counterpart the electron. It is very significant that in no analysis of positive rays so far performed have we been able to discover a particle of mass less than that of the hydrogen atom. This direct result, supported as it is by many less direct lines of evidence, leads logically to the conclusion that the hydrogen positive ray, i.e. the positively charged part remaining when an electron is detached from a neutral hydrogen atom, is the atom of positive electricity itself. The name "proton"[1] was suggested for it by Sir Ernest Rutherford at the Cardiff meeting of the British Association in 1920. The charge on a proton is, of course, equal and of opposite sign to that on the electron. Its mass in the free state has been measured directly[2] and is practically identical with that of the neutral atom of hydrogen $1{\cdot}66 \times 10^{-24}$ grs., or 1·007 on the oxygen scale.[3]

88. The Nucleus Atom.—Certain experimental results, notably the scattering of alpha rays, led Sir Ernest Rutherford in 1911[4] to formulate an atom model which has resulted in the most remarkable advances in both physics and chemistry, and is now almost universally accepted as correct in fundamental principle. This is that an atom of matter consists of a central massive nucleus carrying a positive charge which is surrounded, at distances relatively great compared with its diameter, by "planetary" electrons. The central nucleus contains all the positive electricity in the atom, and therefore practically all its mass. The weight of the atom and its radioactive properties are associated with the nucleus; its chemical properties and

---

[1] From Greek πρῶτον first—the primary substance.

[2] P. 67.

[3] *V.* p. 105.

[4] Rutherford, *Phil. Mag.* **41,** 669, 1911.

spectrum, on the other hand, are properties of its planetary electrons. It is clear that in a neutral atom the positive charge on the nucleus must be equal to the sum of the negative charges on the planetary electrons.

89. Moseley's Atomic Numbers.—The scattering experiments mentioned above indicated that the net positive charge on the nucleus (expressed in terms of the natural unit e) was roughly equal to half the atomic weight. Now if we arrange the elements in order of atomic weight, starting with hydrogen, each element will have a position the number of which will be about half its atomic weight. It was suggested by Van den Broek that this atomic number might be equal to the charge on the nucleus. Two years after the formulation of the nucleus atom theory Moseley undertook an investigation of the changes which took place in the wave-length of the X-rays given off when various elements were used in turn as anticathodes. The result of this piece of work, now classical,[1] was the establishment of the most important generalisation in the history of chemistry since Mendeleef's Periodic Law. Discussing a quantity Q related to wave-length Moseley writes :—

"It is at once evident that Q increases by a constant amount as we pass from one element to the next, using the chemical order of the elements in the periodic system. Except in the case of Nickel and Cobalt,[2] this is also the order of the atomic weights. While, however, Q increases uniformly the atomic weights vary in an apparently arbitrary manner, so that an exception in their order does not come as a surprise. We have here a proof that there is in the atom a fundamental quantity, which increases by regular steps as we pass from one element to the next. This quantity can only be the charge on the central positive nucleus, of the existence of which we already have definite proof. Rutherford has shown, from the magnitude of the scattering of α particles by matter, that the nucleus carries a positive charge approximately equal to that of A/2 electrons when A is the atomic weight. Barkla, from the scattering of X-rays by matter, has shown that the number of electrons in an

---

[1] Moseley, *Phil. Mag.*, **26**, 1031, 1913.
[2] Cf. Barkla, *Phil. Mag.*, **14**, 408, 1907.

atom is roughly A/2, which for an electrically neutral atom is the same thing. Now the atomic weights increase on the average by about 2 units at a time, and strongly suggest the view that N increases from atom to atom always by a single electronic unit. We are therefore led by experiment to the view that N is the same as the number of the place occupied by the element in the periodic system. This atomic number is then for H 1, for He 2, for Li 3—for Ca 20—for Zn 30, etc. This theory was originated by Broek[1] and since used by Bohr. We can confidently predict that in the few cases in which the order of the atomic weights A clashes with the chemical order of the periodic system the chemical properties are governed by N, while A itself is probably some complicated function of N."

Subsequent work has supported in an unquestionable manner the ideas so expressed by Moseley. That the number of the element in the order of the periodic table is actually the same as the positive charge on the nuclei of its atoms, expressed of course in terms of the natural unit of electric charge e, has been proved by direct experiment for some of the heavier elements. The recent work of Chadwick[2] leaves little room for doubt on that point. At the other end of the scale all the known properties of hydrogen point to the conclusion that its atomic number is 1; its exceptional atomic weight, as will be seen later, is itself strong corroborative evidence of this.

A complete table of the elements with their Atomic Numbers, Atomic Weights and isotopes (where these are known) is given on page 142.

From Moseley's law of atomic numbers the explanation of the empirical rule of radioactive transformation given on page 11 follows at once. An alpha particle carries two positive charges, a beta particle one negative one. If therefore the atom of a radioactive substance emits one alpha particle from its nucleus it naturally descends two units in atomic number, that is moves back two places in the periodic table. If on the other hand it emits one beta particle it clearly moves forward one place, for by the operation the nucleus has acquired one additional charge.

---

[1] Van den Broek, *Phys. Zeit.* **14,** 33, 1913.

[2] Chadwick, *Phil. Mag.,* **40,** 734, 1920.

90. The Bohr Atom.—In this atom model the electrons outside the nucleus are supposed to be in a state of continual revolution about it, like planets round the sun. This rotation is considered to take place in orbits defined in a very special manner by means of a "quantum relation." This postulates that when, and only when, an electron changes its orbit, radiation is given out and the energy acquired by the change of orbit is entirely given off as radiation of frequency ν where the change of energy equals $h\nu$—where h is Planck's quantum or element of action ($6{\cdot}55 \times 10^{-22}$ C.G.S.).[1] This theory lends itself to exact mathematical analysis but unfortunately it can only be worked out adequately for the two simplest cases, the neutral hydrogen atom and the singly charged helium atom. Here, however, its success is most remarkable; for not only is it possible to calculate by its means the wave length of the chief series lines of the hydrogen spectrum, to an accuracy almost unprecedented in physics, but, by applying the relativity correction for change of mass with velocity to the rotating electron, the fine structure of the lines and the effects of electric and magnetic fields have been predicted with the most astonishing exactness by Sommerfeld, Epstein and others.[2] Bohr has recently expressed the hope of extending his theory to heavier atoms by means of a new device which he terms the principle of "correspondence."[3]

91. The Lewis Langmuir Atom.—This form of atom model was primarily designed to afford some theoretical basis for the numerous general qualitative properties of elements and their compounds. In it the electrons outside the nucleus are supposed to be at rest at, or vibrating about, definite points. The first two electrons will form a pair, the next eight will tend to set in positions corresponding to the eight corners of a cube, or some other solid figure, and so on. In this way we shall get a series of shells or sheaths one outside the other. Langmuir has recently[4] reduced his postulates to the following three :—

(1) The electrons in atoms tend to surround the nucleus in

---

[1] Bohr, *Phil. Mag.* **36,** 1, 476, 857, 1913.

[2] Sommerfeld, *Atombau and Spektrallinien,* Brunschweig, 1921.

[3] Bohr, *Nature,* **107,** 104, 1921.

[4] Langmuir, *Brit. Assoc. Edinburgh meeting,* 1921.

successive layers containing 2, 8, 8, 18, 18, 32 electrons respectively.

(2) The atoms may be coupled together by one or more "duplets" held in common by the complete sheaths of the atoms.

(3) The residual charge on the atom and on each group of atoms tends to a minimum.

This atom model is not amenable to mathematical treatment, but it has been exceedingly successful in accounting for the general chemical qualitative properties of many of the elements and in predicting those of their compounds.

92. Diagrammatical representation of atoms of Isotopes and Isobares.—The accompanying diagrams (Fig. 16) are intended to indicate the sort of arrangements which may take place in atoms. The small dark circle is the nucleus, the number of protons and electrons comprising it being indicated by the numerals. The electrons outside the nucleus are indicated by small light circles.

(1) is an atom of atomic weight 6. Its nucleus contains 6 protons and 3 electrons, hence its atomic number is 3. It is in fact the atom of the lighter isotope of lithium of atomic weight 6, Li^6. To be electrically neutral it must have 3 electrons outside the nucleus. Now the principles underlying Langmuir's first postulate are derived from the Periodic Table and are certainly correct. Langmuir explains this by saying that the first two of these electrons will form an innermost ring or shell of two. This shell being now complete, any more electrons will go outside and start the next shell of eight, so we indicate this by putting the third electron in a circle of greater diameter.

Now suppose we add one electron and one proton to this atom. If both enter the nucleus we shall get the configuration represented by (2) The nuclear charge is unaltered, so that the arrangement of the exterior electrons will be precisely the same. It follows that all properties depending on these electrons such as atomic volume, spectrum, chemical properties, etc., will be quite unaltered. But the weight of this atom is now 7, so it is an isotope of lithium ; it is actually the atom of the heavier constituent Li^7. (1) AND (2) ARE ISOTOPES.

But now suppose we add a proton and an electron to (1) so that the proton only enters the nucleus and the electron remains outside as shown at (3) We shall now have a charge 4 on the nucleus and two electrons in the outer ring. The chemical properties of such an atom, if it could exist, would be completely different from those of lithium, but would be identical with those of beryllium, of which it would be an isotope. But its mass is clearly identically the same as that of (2) so that (2) AND (3) ARE ISOBARES.

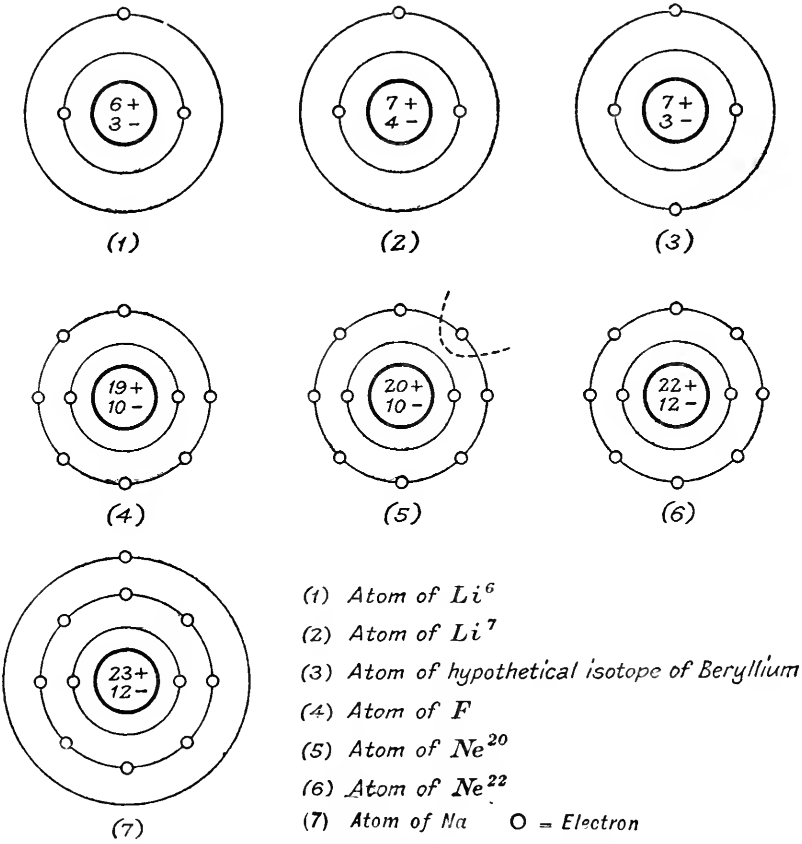


FIG. 16.—Diagrammatic Representation of Nucleus Atoms. The planetary electrons are shown as lying on plane circles, the first containing 2, the second 8 and so on. The dark circle is the nucleus and the + and − charges within it are indicated by figures. (1) and (2) are Isotopes. (2) and (3) are Isobares and (5) and (6) are Isotopes.

In the same way (4) will be recognised as the atom of fluorine (5) and (6) as the atoms of the two isotopes of neon and (7) as the atom of sodium.

93. The relation between Isotopes and Elements in the same Group.—As far as can be seen the chemical properties by which the elements are divided into groups depend practically entirely on the outermost shell of electrons, which are therefore called valency electrons. Now consider all that part called by Langmuir the kernel of the atom lying within the shell of these valency electrons. The movements or configuration of the outermost electrons will depend in the first degree on the charge on the kernel, which may be looked upon as a virtual nucleus. The kernels of atoms (1) and (7) both have the same net charge 1, so that the elements they represent should have many chemical similarities. These they certainly have as both are alkali metals. In general the atoms of elements belonging to the same group chemically have the same number of electrons in the outer shell and the same net charge on the kernel. On this view it will be seen that the similarity of isotopes may be regarded as the extreme limiting case of the similarities long observed between elements of the same chemical group.

94. Abnormal compounds formed by charged atoms.—The tendency of elements to form compounds with each other, that is the property with which the idea of valency is associated, is ascribed to the tendency of the atom to complete its outer shell. This it can do either by parting with the electrons in this shell and so promoting the next inner completed shell to outer position, or by sharing the electrons in the atom of another element so that they fill the gaps in its own outer shell. We have already alluded to the success which has attended this idea in explaining valency and the properties of chemical compounds. For the present argument it will be enough if it is understood that lithium and sodium (1) (2) (7) will very readily part with their solitary valency electron and become positively charged, i.e., will be strongly electropositive elements with valency + 1 ; whereas a fluorine (4) will have an equally powerful tendency to take up an electron and become negatively charged and so will be a strongly electronegative element with valency — 1. Both of these tendencies will be satisfied if (4) and (7) combine forming the compound molecule NaF, for the outer electron of (7) will enter the outer shell of (4) thus forming two complete shells of eight (Langmuir's octets). We trace the tendency of the atom of fluorine, or any other halogen, to form compounds with the atom of an electro-positive element, or with the atom of hydrogen, to the fact that it has one too few electrons in its outer shell.

Now the only way we can give a positive charge to an atom of neon (5) or (6) is by knocking one or more electrons out of its outer shell. Suppose we remove one from (5) as indicated by the dotted line. (5) now will have a similar outer shell to (4) and a valency — 1, so we may expect that atoms of the inert gases carrying a single positive charge will behave chemically in a similar manner to neutral halogen atoms and will therefore be capable *so long as they are charged* of forming hydrides. This very important idea was first suggested by Sir J. J. Thomson in connection with the charged atoms of chlorine[1] and certainly supplies a very satisfactory explanation of the very abnormal hydrides of inert gases and compounds such as OH_3 discovered in positive rays. The line at 41 (Spectrum VI, Plate III) is probably to be put down to a charged hydride of argon of this type. Exceedingly faint lines at 5 in the case of helium, and 21 in the case of neon, are probably to be ascribed to similar abnormal compound (HeH) and (NeH) respectively. In the case of atoms carrying more than one charge it can be generally stated that each positive charge given to an atom will increase its negative valency by one.

95. The failure of the additive law in respect to mass.— We have seen that, for velocities small compared with that of light, the masses of the proton and the electron may be regarded as universal constants. If the additive law were strictly true as regards the summation of their masses it is clear that any mass whatever, whether it were that of an atom or a molecule, a planet or a star, or even the universe itself could be expressed in the form NM where N is a pure integer

---

[1] J. J. Thomson, *Proc. Roy. Soc.* **99A**, 90, 1921.

and M the mass of the neutral system 1 proton + 1 electron (= the atom of hydrogen). The simplicity of this idea, which is Prout's theory in the language of modern physics, is extremely attractive; but we know it to be false, for although the discovery of isotopes has removed the difficulty of the grosser fractions associated with such elements as neon and chlorine, we are still left with the more minute but none the less real one associated with hydrogen itself. To explain this the additive law must be qualified by some such reasoning as is contained in the following paragraph.

96. The explanation of the fractional mass of the hydrogen atom by the hypothesis of "packing."—According to generally accepted views the proton and the electron possess *mass*, or what on the relativity theory is regarded as the same thing, *weight*, by virtue of the energy in the electromagnetical field which surrounds them. It can easily be shown on classical lines that if we give it a spherical form a charge e spread uniformly over the surface of the sphere will have a mass m when its radius a is such that $m = \frac{2}{3}\frac{e^2}{a}$; hence to give the electron its proper mass its charge must be compressed to a sphere of diameter about $3{\cdot}8 \times 10^{-13}$ cm. By the same argument the proton will be nearly two thousand times smaller and have a diameter $2{\cdot}06 \times 10^{-16}$ cm. The extreme range of the diameter of atoms themselves is $1 - 5 \times 10^{-8}$ cm., so that it will at once be realised that the structure of an atom is an exceedingly open one, even more so than that of our solar system.

Now it can be shown that if we bring two charges of opposite sign sufficiently close together their fields will affect each other in such a way that the mass of the system will be reduced. This effect is quite inappreciable for distances comparable with the diameter of an atom, but begins to make itself felt when the distance apart is of the order of the size of the electron itself as given above. The nucleus of the atom of an ordinary element (not hydrogen) contains both protons and electrons and is very small compared with the atom itself. Its dimensions can be roughly determined by actual experiment in the case of the heavy elements and are found to be so small that even to get in the electrons alone these would have to be packed very closely together. Such a nucleus will contain more protons than electrons, roughly twice as many, so that it may be regarded as practically certain that :—*In the nuclei of normal atoms the packing of the 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.*

The nucleus of a hydrogen atom consists of one single free proton, its planetary electron is too far away to cause any effect so that it is clear that we shall find the mass associated with the atom of hydrogen greater than one-fourth the mass of a helium atom or one-sixteenth the mass of an oxygen atom. The mass lost when four free protons and two free electrons are packed close together to form a helium nucleus (No. 9, p. 106) is roughly 0·7 per cent. of the whole and it can be calculated that, if we take the value of the diameter of the electron given above, the protons must approach nearer than half of this to give so large a reduction. This means that the charges must be so closely packed that the electrons are actually deformed.

The whole number rule may now be simply translated into a statement that the mean packing effect in all atoms is approximately constant, and the unit of mass 1 when $O=16$ will be (mass of a packed proton) + $\frac{1}{2}$ (mass of free electron) + $\frac{1}{2}$ (mass of packed electron). The whole number rule is not, and never was supposed to be, mathematically exact, for this would imply an identical packing effect in the case of all atoms, an exceedingly improbable supposition. It is almost certain that atoms of some elements, such as nitrogen, weigh slightly more than a whole number (looser packing) while those of others such as caesium or iodine may weigh slightly less (closer packing). The limit of accuracy so far attained in mass-spectrum measurement is not sufficient to detect a change of the order expected, except in the case of hydrogen, where the variation in mass is exceptionally high.

97. The structure of the nucleus.—The manner in which the units of electricity are arranged in the nucleus of an atom has received a good deal of attention from theorists but ideas on this subject are almost entirely of a conjectural character. Thus Harkins[1] has proposed a constitutional formula for the nuclei of all the elements. In this, besides electrons and protons, he uses as building units α particles (4 protons + 2 electrons) of mass 4, and hypothetical units of mass 3 with a single positive charge (3 protons + 2 electrons). The matter has been more recently discussed and nucleus models suggested by Rutherford,[2] E. Gehrcke[3] and others.

The fact that the helium nucleus is almost exactly an integer on the oxygen scale—that is to say helium has approximately normal packing—gives a distinct balance of probability that helium nuclei actually exist as such in the nuclei of normal elements. In support of this idea it has been stated that the presence of helium nuclei inside the nuclei of radioactive atoms is definitely proved by the ejection of α particles by the latter. In the writer's opinion this is much the same as saying that a pistol contains smoke, for it is quite possible that the α particle, like the smoke of the pistol, is only formed at the moment of its ejection. Brösslera[4] defends this view and points out that if the alteration from looser to closer packing of the charges forming the particle is at all large energy will be liberated amply sufficient for the purpose of detaching it and giving it the energy of an α ray. The reason to expect that this energy will be set free will be described in the next section. Brösslera's suggestion that in the nuclei of radioactive atoms there are loosely bound protons and electrons and that these, given something of the nature of a certain exact and instantaneous correlation, might combine to form an α particle is in good accordance with the most reasonable theory of radioactive disintegration, which was first put forward by Lindemann.[5]

There are therefore two different ideas which we may regard

---

[1] Harkins, *Phys. Rev.*, **15**, 73, 1920.

[2] Rutherford, *Proc. Roy. Soc.*, **97A**, 374, 1920.

[3] Gehrcke, *Phys. Zeit.*, **22**, 151, 1921.

[4] Brösslera, *Rev. Chim.*, **1**, 42, 74, 1921.

[5] Lindemann, *Phil. Mag.*, **30**, 560, 1915.

as working hypotheses. According to the first the nuclei of atoms consist of helium nuclei, or a particles, held together in some way so that their packing effect *upon each other* is small; and, in the case of atoms not having a mass of the type $4n$, additional protons and electrons. According to the second we only have to suppose that the *mean* packing of all the charges in the nucleus is such as will account for the whole number rule with sufficient exactness, but that the actual arrangement of the protons and electrons need not necessarily be at all similar to that in a helium nucleus.

The experimental evidence is, so far, definitely in favour of the first of these views. In their remarkable work on the disintegration of light atoms by the collision of swift a rays Rutherford and Chadwick [1] show that as the result of such collisions swift hydrogen rays, i.e. free protons, are liberated from the atoms of boron, nitrogen, fluorine, sodium, aluminium and phosphorus. They point out that the masses of the atoms of all these elements are of the types $4n + 2$ and $4n + 3$. The effect is not obtained from atoms of the type $4n$ so that this result suggests that in these the protons are already all bound together to form helium nuclei.

98. Cosmical effects due to change of mass.—It has long been known that the chemical atomic weight of hydrogen was greater than one quarter of that of helium, but so long as fractional weights were general there was no particular need to explain this fact, nor could any definite conclusions be drawn from it. The results obtained by means of the mass-spectrograph [2] remove all doubt on this point, and no matter whether the explanation is to be ascribed to packing or not, we may consider it absolutely certain that if hydrogen is transformed into helium a certain quantity of mass must be annihilated in the process. The cosmical importance of this conclusion is profound and the possibilities it opens for the future very remarkable, greater in fact than any suggested before by science in the whole history of the human race.

We know from Einstein's Theory of Relativity that mass

---

[1] Rutherford and Chadwick, *Phil. Mag.*, **42**, 809, 1921.

[2] *V.* p. 70.

and energy are interchangeable[1] and that in C.G.S. units a mass m at rest may be expressed as a quantity of energy mc^2, where c is the velocity of light. Even in the case of the smallest mass this energy is enormous. The loss of mass when a single helium nucleus is formed from free protons and electrons amounts in energy to that acquired by a charge e falling through a potential of nearly thirty million volts. A swift α ray has an energy of three to four million volts so that the change of packing suggested by Brösslera need not be nearly so great to provide the energy needed. If instead of considering single atoms we deal with quantities of matter in ordinary experience the figures for the energy become prodigious.

Take the case of one gramme atom of hydrogen, that is to say the quantity of hydrogen in 9 c.c. of water. If this is entirely transformed into helium the energy liberated will be

$$\cdot 0077 \times 9 \times 10^{20} = 6\cdot 93 \times 10^{18} \text{ ergs.}$$

Expressed in terms of heat this is $1\cdot 66 \times 10^{11}$ calories or in terms of work 200,000 kilowatt hours. We have here at last a source of energy sufficient to account for the heat of the Sun.[2] In this connection Eddington remarks that if only 10 per cent. of the total hydrogen on the Sun were transformed into helium enough energy would be liberated to maintain its present radiation for a thousand million years.

Should the research worker of the future discover some means of releasing this energy in a form which could be employed, the human race will have at its command powers beyond the dreams of scientific fiction; but the remote possibility must always be considered that the energy once liberated will be completely uncontrollable and by its intense violence detonate all neighbouring substances. In this event the whole of the hydrogen on the earth might be transformed at once and the success of the experiment published at large to the universe as a new star.

---

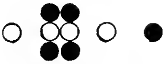
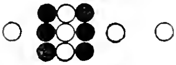
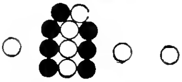
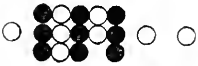
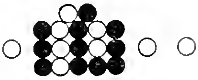
[1] Eddington, *Time, Space and Gravitation*, p. 146, Cambridge, 1920.

[2] Eddington, *Brit. Assoc. address*, 1920; Perrin, *Scientia*, Nov., 1921.

99. The stable systems of protons and electrons known to occur.—Starting with our standard bricks, the protons and electrons, we may make, theoretically at least, an infinity of systems by the combination of any number of each. It is interesting to consider the systems actually occurring in practice, that is to say those which are sufficiently stable to give definite evidence of their existence. The following table gives, in order of mass, the first twenty-four known. Where the circles representing the charges touch each other, to form nuclei, the packing is extremely close, where they do not touch they are to be taken as distant thousands of times further from each other. The masses of the first twelve are deduced as follows :—The most accurate value for the chemical atomic weight of hydrogen is 1·0077 (0 = 16), and as it is very improbable that it consists of isotopes we take this as the mass of a neutral hydrogen atom. The mass of the electron is 0·00054 and as the packing effect is nil we arrive at the figure 1·0072 for the mass of the proton, and this agrees within the experimental error with that directly determined by the mass-spectrograph. The most probable value of the mass of a neutral helium atom is 4·00(0) we will assume the last figure for the sake of simplicity. The masses of (13) to (24) are less accurately known.

The stability, where known, is expressed in volts and represents the potential through which a charge *e* must fall in order to acquire sufficient energy to disrupt the particular configuration concerned. This is the ionisation potential in the case of atoms.

Number of diagram.		Atomic Number.	Nuclear Constitution.	Charge.	Mass.	Stability.	Description.
1		0	0	–1	0·00054	—	Electron
2		1	1+	+1	1·0072	—	Proton or positively charged H atom
3		1	1+	0	1·0077	14	Neutral H atom
4		1	1+	–1	1·0082		Negatively charged H atom
5		1	1+	+1	2·0149		Positively charged H molecule
6		1	1+	0	2·0154	4·3	Neutral H_2 molecule
7		1	1+	+1	3·0226	small	Positively charged H_3
8		1	1+	0	3·0231	small	Neutral H_3
9		2	4+2–	+2	3·999	>3x 10^6	Doubly charged helium atom or alpha ray
10		2	4+2–	+1	3·999	55	Singly charged helium atom
11		2	4+2–	0	4·000	25	Neutral helium atom.

Number of diagram.		Atomic Number.	Nuclear Constitution.	Charge.	Mass.	Stability.	Description.
12		2	4+2 –	+1	5·007		Positively charged HeH
13		3	6+3 –	+1	6·0		Positively charged Li^6 atom
14		3	6+3 –	0	6·0	4·9*	Neutral Li^6 atom
15		3	7+4 –	+1	7·0		Positively charged Li^7 atom
16		3	7+4 –	0	7·0	4·9*	Neutral Li^7 atom
17		3	6+3 –	0	6·0(07)		Neutral Li^6H molecule
18		3	7+4 –	0	7·0(07)		Neutral Li^7H molecule
19		4	9+5 –	+1	9·0		Positively charged Be atom
20		4	9+5 –	0	9·0	3·3*	Neutral Be atom
21		5	10+5 –	+2	10·00		Doubly charged B^{10} atom
22		5	10+5 –	0	10·00		Positively charged B^{10} atom
23		5	10+5 –	0	10·00		Neutral B^{10} atom
24		5	11+6 –	+2	11·00		Doubly charged B^{11} atom

* Calculated from frequency of radiation.

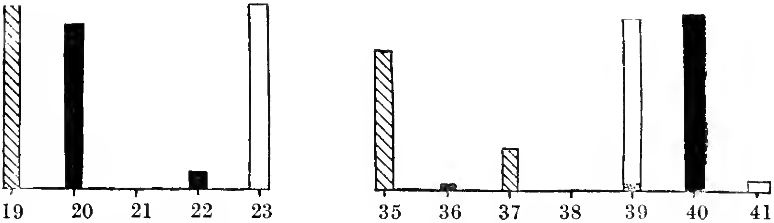
CHAPTER IX

ISOTOPES AND ATOMIC NUMBERS

100. The relation between chemical atomic weight and atomic number.—Inasmuch as it is now recognised to be in general merely a statistical mean value the importance of the chemical atomic weight has been greatly reduced by the discovery of isotopes. Its position as the natural numerical constant associated with an element has been taken by the atomic number, though from the point of view of chemical analysis the chemical atomic weight is just as important as it ever was.

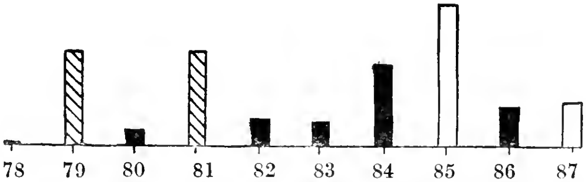
The possibility of anomalies in the order of the elements in the periodic table when their chemical atomic weights are considered, is now obvious enough. The true weights of the atoms as directly determined, are so intermingled in the order of the natural numbers and the proportions present in complex elements so varied that such anomalies are bound to occur, indeed it is rather surprising there are not more.

The following table (Fig. 17) shows the masses of the isotopes of three groups of elements now completely investigated. The approximate proportions present are indicated by the heights of the columns; plain for the alkali metals, black for the inert gases, and hatched for the halogens. The anomalous order of argon and potassium is at once seen to be due to the fact that whereas the heavier constituent of argon is present in much the greater proportion, in potassium the reverse is the case. Had the proportions of heavier and lighter isotopes been similar in each case the atomic weight of potassium would have been greater instead of less than that of argon.

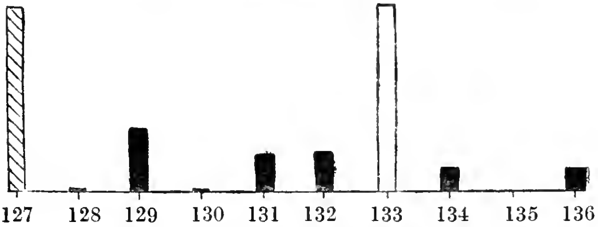


Fluorine (9) Neon (10)
Sodium (11)

(Chlorine 17) Argon (18)
Potassium (19)



Bromine (35) Krypton (36) Rubidium (37).



Iodine (53) Xenon (54) Caesium (55)

FIG. 17.—Isotopes of the Halogens, the inert gases and the alkali metals.

101. Statistical relations exhibited by elements and their isotopes.—Although our knowledge of true atomic weights is far from complete, for out of eighty-seven existing elements only twenty-seven have been analysed, of which thirteen are simple, interesting relations have already become clear which are stated in the form of rules as follows :—

In the nucleus of an atom there is never less than one electron to every two protons. There is no known exception to this law. It is the expression of the fact that if an element has an atomic number N the atomic weight of its lightest isotope cannot be less than 2N. Worded as above, the exception in the case of hydrogen is avoided. True atomic weights corresponding exactly to 2N are known in the majority of the lighter elements up to A^{36}. Among the heavier elements the difference between the weight of the lightest isotope and the value 2N tends to increase with the atomic weight; in the cases of mercury it amounts to 37 units. The corresponding divergence of the *mean* atomic weights from the value 2N has of course been noticed from the beginning of the idea of atomic number.

The number of isotopes of an element and their range of atomic weight appear to have definite limits. Since the atomic number only depends on the *net* positive charge in the nucleus there is no arithmetical reason why an element should not have any number of possible isotopes. An examination of the tables of results given on p. 89 and at the end of the book show that so far the largest number determined with certainty is 6 in the case of krypton. It is possible that xenon has even more, but the majority of complex elements have only two each. The maximum difference between the lightest and heaviest isotope of the same element so far determined is 8 units in the cases of krypton and xenon. The greatest proportional difference, calculated on the lighter weight, is recorded in the case of lithium, where it amounts to one-sixth. It is about one-tenth in the case of boron, neon, argon and krypton.

The number of electrons in the nucleus tends to be even. This rule expresses the fact that in the majority of cases even atomic number is associated with even atomic weight and odd with odd. If we consider the three groups of elements, the halogens, the inert gases and the alkali metals, this tendency is very strongly marked. Of the halogens—odd atomic numbers—all 6 (+ 1 ?) atomic weights are odd. Of the inert gases—even atomic numbers—13 (+ 2 ?) are even and 3 odd. Of the alkali metals—odd atomic numbers—7 are odd and 1 even. In the few known cases of elements of the other groups the preponderance, though not so large, is still very marked and nitrogen is the only element yet discovered to consist entirely of atoms whose nuclei contain an odd number of electrons.

A further interesting result is the *absence of isobares.* So far none have been definitely identified, but it is quite obvious that in the cases of elements such as calcium and selenium they must exist, for the supply of integers in the region of their atomic weights have been exhausted by the needs of other elements.

A table of the first 40 natural numbers and the true atomic weights corresponding to them is given in Fig. 18. The gaps are particularly interesting and seem to show no semblance of regularity. It is very clear that many more experimental results will have to be obtained before any satisfactory theory for the occurrence of these, or of the other laws, is to be formulated.

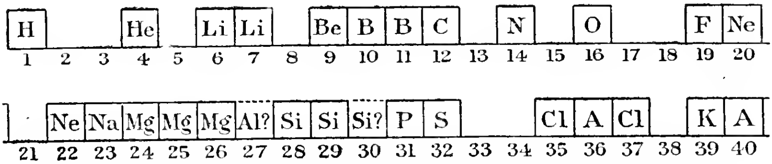


FIG. 18.—The first 40 natural numbers, showing those occupied by atomic weights of known elements.

102. The preponderance of elements of even atomic number.—In discussing the nuclear structure of elements the question of their relative abundance in nature is one of great interest. This may be estimated by direct chemical analysis of the Earth's crust, and such extra-terrestrial sources as are available in the form of meteorites. The spectroscope will tell us what elements are present in the stars, but unfortunately it does not give much direct information as to their relative quantities.

On this question we can classify—to use biological terms —either by *individuals* or by *species*. We may examine the percentage composition, which will give a measure of the total number of individual atoms of each element present, or we may inquire into the number of different nuclear species which occur and classify them without respect to their individual abundance.

A very valuable discussion from the first point of view has been published by Harkins,[1] who considers the percentage composition of meteorites and of parts of the Earth's crust. He demonstrates in a most convincing manner that there are

---

[1] Harkins, *Jour. Amer. Chem. Soc.*, **39,** 856, 1917.

immensely more atoms of elements of even atomic number. This interesting preponderance can, with a reasonable amount of probability, now be extended to even atomic weight, by the statistics given in the preceding paragraphs, but it will not be certain until the constitution of certain abundant elements such as iron has been actually determined.

The second point of view can be examined by means of the atomic weights of the radioactive isotopes and also by the true atomic weights given by the mass-spectra. In both cases nuclear systems of even atomic number are found to predominate. The mass-spectra of 13 elements of even, and 14 elements of odd atomic number indicate 32 isotopes of even atomic number and 20 of odd. The average element of even atomic number has therefore 2·5 isotopes to 1·4 for each element of odd atomic number.

The table on p. 15 shows that among the radioactive isotopes the preponderance is greater—32 as against 10—but it is possible that the former figure may include some atomic systems absolutely identical though of different origin.

103. The constancy of chemical atomic weights.—One of the first difficulties in the way of accepting the idea of the complex constitution of an element such as chlorine was the constancy of its atomic weight. This had been determined by many different observers using different methods and the results were always the same within a very small experimental error. This difficulty may be met, in the first place, by noting that the vast majority, if not all, of the really accurate values were obtained from chlorine which must have been originally derived from the sea. The sea has been mixed for so long that it would be absurd to expect to find chlorines of different chemical atomic weights in it. Had ordinary galena been the only source of lead used in the atomic weight determinations given on page 16 no difference would have been found. It was only by examining the lead from extraordinary radioactive sources that the results were obtained which gave such definite and valuable support to the theory of isotopes.

The atomic weight of chlorine from sources other than the sea is now receiving the attention of chemists, though it is naturally very difficult to be at all sure that any known source of chlorine is not of marine origin. Mlle. Irene Curie [1] has examined the atomic weight of chlorine from three minerals whose marine origin seems unlikely. The values obtained from a sample of sodalite (sodium aluminium chlorosilicate) from Canada, and from a sample of calcium chlorophosphate from Norway agree with the value for chlorine from sea-water. The value 35·60, for chlorine from a sample of sodium chloride from a desert region in Central Africa was slightly high.

The comparison of the atomic weights of terrestrial and meteoric nickel made by Baxter and Parsons [2] is interesting in this connection. As a mean of nine determinations with the terrestrial material the figure 58·70 was found, whilst three experiments with meteoric nickel gave 58·68. The standard value found by Richards and Cushman was 58·68 (Ag = 107·88). The difference found between terrestrial and meteoric nickel is considered to be within the limits of experimental error, but further comparisons are to be made.

The writer regards these negative results as having a cause probably much more fundamental than the mere mechanical mixing of the different constituent isotopes during the history of the body containing them, namely a constancy of proportion during the evolution of the elements themselves. This will be considered later. The case of the radioactive leads is entirely exceptional. These substances have been produced continuously during the history of the earth's crust and are being so produced to-day. Although ordinary lead may consist of isotopes—which is practically certain—and these isotopes may be identical in every respect with those produced in the last stage of radioactive disintegration, yet there is no reason whatever to assume that ordinary lead is itself the accumulated result of these processes. It takes its place among the other ordinary elements and would doubtless have done so had thorium and uranium never existed.

104. The agreement between the chemical atomic weight and the mean atomic weight deduced from the mass spectrum.—The mean atomic weight of the isotopes

---

[1] I. Curie, *Compt. Rend.* **172,** 1025, 1921.

[2] Baxter and Parsons, *Jour. Amer. Chem. Soc.*, **43,** 507, 1921.

of a complex element can be calculated if the relative intensities of their lines in the mass-spectrum is known. This has been directly measured by Dempster.[1] The charged particles of isotopes of the same element are practically certain to affect the photographic plate to the same extent as each other, hence we can obtain a rough estimate of their relative proportion by comparing the intensities of the lines. If this is done it is found that the great majority of the elements so far tested give mean results in good agreement with the accepted chemical values. The following table gives the data concerning four in which the difference is noteworthy :—

Element.	Atomic Weight.	Mean from Mass-spectrum.	Difference.	Per cent. Difference.
Boron	10·90	10·75±0·07	0·15	1·37
Krypton . . .	82·92	83·5 ±0·3	0·6	0·72
Xenon . . .	130·2	131·3 ±0·3	1·1	0·85
Caesium . . .	132·81	133 ±0·3	0·2	0·05

The case of boron is the most difficult to account for. The masses of its isotopes 10 and 11 certainly do not differ from integers by more than one or two parts in a thousand. The ratio of the intensities of their second order lines 5 and 5·5 (and there were no other substances present which could possibly give such lines) is equally certainly not as high as 9 : 1. It was for this reason that a third isotope 12 was suspected, but as no evidence of this has been found it seems most probable that the chemical atomic weight is still slightly too high.

The atomic weights of krypton and xenon are not of course chemical in the ordinary sense, as they are deduced direct from density determinations. Any trace of the impurity most likely to be present, argon in the first case, krypton in the second, would tend to make the densities too low, and this appears the most likely explanation.

In the case of caesium the chemical result may be correct, for the probable error in the determination of mass is at least as large as the discrepancy. On the other hand caesium

---

[1] *V.* p. 81.

appears to be a simple element, in which case its chemical atomic weight must represent the true weight of its atoms. Any error in this figure would probably be of the sign suggested, for it is the heaviest member of its chemical group. If, however, as is possible, the true mass of its atom differs from an integer by as much as 0·2 it is a fact of the greatest interest.

105. The meaning of the word "element."—The exact idea conveyed by the word "element" in chemistry and physics has given rise to endless difficulties in the past. In this connection Crookes in 1886 sums up the matter as follows :—"Of the attempts hitherto made to define or explain an element, none satisfy the demands of the human intellect. The textbooks tell us that an element is 'a body which has not been decomposed'; that it is 'a something to which we can add, but from which we can take away nothing,' or 'a body which increases in weight with every chemical change.' Such definitions are doubly unsatisfactory: they are provisional, and may cease to-morrow to be applicable to any given case. They take their stand, not on any attribute of things to be defined, but on the limitations of human power; they are confessions of intellectual impotence."

There was good reason for this dissatisfaction. The discovery ten years later of the electron, and the subsequent electrical theory of matter robbed the word of any pretence to its original meaning; for although Ramsay attempted to introduce into chemistry electricity itself as an element, it soon became obvious that this extension was unsuitable. The discovery of isotopes brings us face to face with two possible alternatives. The first is to call each isotope, as it is discovered, a new element. The second is to fix the word precisely, now and for the future, as meaning a substance with definite chemical and spectroscopic properties which may or may not be a mixture of isotopes—in other words to associate it exclusively with the conception of atomic number. On this view there would be, corresponding to Moseley's numbers, 92 possible elements, of which 87 are known.

If we adopt the first of these alternatives a new word will be necessary to express such substances as chlorine or magnesium, hitherto called elements, and also the word element would mean something entirely different from what it has meant in all the chemical and physical literature of the past century. It would moreover be still subject to alterations in the future.

In the opinion of the writer the second alternative—the association of element with atomic number—is much the more preferable. The difficulties arising from it are practically confined to the radioactive substances which can differ from one another even when their atomic numbers and atomic weights are identical. This is not very serious, for the radioactive elements are in a class by themselves and the special nomenclature already applied to them could be retained or revised as convenient without affecting that of general chemistry.

106. Disintegration theory of the evolution of the elements.—A theory has been put forward by some writers that all the elements occurring in nature are the result of radioactive disintegrations of the ordinary type, but continued far beyond the ordinary limit observed at present. For instance, if we continue the α ray changes of the thorium series far enough we shall ultimately reach helium. The emission of an α particle is the only change known to occur which alters the atomic weight and it always does so by 4 units at a time. Hence from thorium we shall get a series of elements or isotopes of atomic weights from 232 to 4 of the general type $4n$. Uranium in the same way will yield a similar series of the type $4n + 2$. In order to obtain isotopes of odd atomic weight it is necessary to postulate parent elements of the type $4n + 1$ and $4n + 3$.

Using hypotheses based on this general idea Van den Broek,[1] Harkins,[2] Kohlweiler,[3] Kirchoff [4] and others have built up the most elaborate systems of isotopes.

---

[1] Van den Broek, *Phys. Zeit.*, **17**, 260, 579, 1916; **22**, 164, 1921.

[2] Harkins and Wilson, *Jour. Am. Chem. Soc.*, **37**, 1367, 1915; Harkins and Hall, *ibid.*, **38**, 169, 1916; Harkins, *Phys. Rev.*, **15**, 73, 1920; *Nature*, **105**, 230, 1920; *Jour. Amer. Chem. Soc.*, **42**, 1956, 1920; *Phil. Mag.*, **42**, 305, 1921.

[3] Kohlweiler, *Zeit. für physikal. Chem.*, **94**, 513, 1920; *Phys. Zeit.*, **21**, 311, 543; **22**, 243, 1921.

[4] Kirchoff, *ibid.*, **21**, 711, 1920.

The writer regards this view as unlikely and misleading. In the first place it does not appear to succeed in its objects. As an explanation of how the elements may have been evolved it starts with at least four elements as complicated as any known to exist, which does not advance the inquiry very much. On the other hand it may be used to predict the atomic weights of the isotopes composing known elements, and a great many predictions of this kind have been made. Here, though the measure of its success has varied to some extent with the particular modification of the theory employed, it has never been worthy of serious consideration. In cases where two or three isotopes of a given element were predicted they proved as often wrong as right, and when the number of isotopes of integral atomic weights was so large that some agreements were inevitable the argument obviously loses all its force.

Another objection is that radioactive transformations do not continue, as far as we can see, beyond the stage (lead) indicated in the diagrams on p. 15. The lighter elements are definitely not radioactive. The radioactivity of potassium and rubidium is exceedingly small and its nature doubtful; in any case it is best ascribed to minute vestiges of radioactive isotopes, not to feeble radioactivity of the main constituents. It seems therefore more reasonable, for the present, to regard the property of radioactivity as absent entirely from the inactive elements than to suppose it present but too weak to be detected. It must not be gathered from these remarks that it is considered impossible to imagine physical conditions violent enough to disrupt the nuclei of light atoms, but rather that the mechanism causing such disruption need not be similar in any way to that causing normal radioactivity.

107. Crookes' theory of the evolution of the elements.—A more attractive theory than the one given above is that the complex atoms of matter have been evolved by the aggregation of simpler atoms. This idea has received a good deal of attention in the past. Crookes[1] remarks on it as follows:—

"Let us picture the very beginnings of time, before geological

---

[1] Crookes, *Brit. Assoc. address*, 1886.

ages, before the earth was thrown off from the central nucleus of molten fluid, before even the sun himself had consolidated from the original *protyle*. Let us still imagine that at this primal stage all was in an ultra-gaseous state, at a temperature inconceivably hotter than anything now existing in the visible universe; so high indeed that the chemical atoms could not yet have been formed, being still far above their dissociation point. In so far as *protyle* is capable of radiating or reflecting light, this vast sea of incandescent mist, to an astronomer in a distant star, might have appeared as a nebula, showing in the spectroscope a few isolated lines, forecasts of hydrogen, carbon and nitrogen spectra.

"But in due course of time some process akin to cooling, probably internal, reduces the temperature of the cosmic *protyle* to a point at which the first step in granulation takes place; matter as we know it comes into existence, and atoms are formed."

This vivid picture may be brought up to date by the substitution of free protons and electrons for the hypothetical protyle. We can imagine regions containing matter where the temperature is so high that not only is the dissociation of atoms from atoms and nuclei from planetary electrons complete but also protons and electrons are in a state of agitation so violent that even the most stable nuclei cannot be formed. We should have here matter of the simplest form we can imagine, or rather of no form at all, simply a more or less neutral electric gas. Such a condition is by no means impossible in our universe and may actually occur during one of those excessively violent catastrophes occurring in far distant space and observed by us as new stars.

By some such cooling process as that suggested by Crookes we easily imagine the free charges combining to form the nuclei of elements. Whether those of heavier elements are formed direct by the charges getting into particular geometrical relations with each other, or whether helium nuclei are formed first and then subsequently coalesce depends on which theory of nuclear structure is adopted. In any case vast quantities of energy will have to be radiated off and this radiation may be of such extremely high frequency that it is capable of disrupting nuclei themselves, so that there might be at this stage rapid and continuous transformations from heavier to lighter nuclei and vice versa.

For the present we are interested in the number of each type of atom which survives. It is obvious that if the conditions of cooling are practically identical throughout the whole mass there is no reason why the composition of the matter produced should vary. If 3 atoms of Cl^{35} are formed to every 1 of Cl^{37} at any one point the same ratio must hold at every point so that a complex element of constant atomic weight will be formed. But it is much more likely that different parts of this primordial mass will undergo their transformations under different rates of cooling, etc., so it is worth while inquiring if variation in the mean atomic weight of a complex element is to be expected.

The quantity of one particular atomic nucleus formed will probably depend (*a*) on the probability of a certain configuration of charges happening as a chance event; (*b*) the stability of the particular nucleus formed as the result of that event. Again to take the case of chlorine each isotope may be regarded as completely stable and the relative quantities formed will simply depend on condition (*a*). Now it is not unreasonable to suppose that this is not seriously affected by different rates of cooling, and in this case the isotopes will be evolved in constant proportion. As we know of no natural process by which the proportion of isotopes can be altered appreciably the complex elements will have to-day the same chemical atomic weight as when they were first formed.

The above argument is of course purely a speculative one, and the conclusion drawn from it would fall to the ground at once if noteworthy differences of atomic weight in a single complex element were found—supposing that element was not the product of a radioactive change—at different points on the earth's surface. It may be worth noting that condition (*a*) suggests that, in general, the lighter atoms will outnumber the heavier ones. In all matter available in nature this preponderance is actually enormous.

If the matter forming the earth ever went through a primordial stage such as that suggested above it certainly did so more than 10^9 years ago. It follows that of the radioactive elements then formed only two, thorium and uranium, will now be found on the earth, for the other radioactive elements existing to-day are of such short period that they must have been formed since. Hence we may divide the *original* elements very simply and definitely into two groups: (1) All the inactive elements, whose nuclei are sufficiently simple to be stable; (2) Thorium and Uranium, whose nuclei are so complex that they are only partially stable.

Other less stable elements *may* have been formed then but there can be no proof of this for they would, in any case, have disappeared long ago, and it is clear that the other radioactive elements now found can all be regarded as formed from the two parent elements in comparatively recent times.

CHAPTER X

THE SPECTRA OF ISOTOPES

108. The Spectra of isotopes.—As has already been stated[1] the first experimental work on the spectra of isotopes was that of Russell and Rossi in 1912 who failed to distinguish any difference between the spectrum of thorium and that of a mixture of thorium and ionium containing a considerable percentage of the latter. The same negative result was obtained by Exner and Haschek.[2] During the fractional diffusion of neon[3] no spectroscopic difference was detected between the heaviest and the lightest fraction, though as the separation was small this negative evidence was not very strong. In 1914 Soddy and Hyman showed that the spectrum of lead derived from thorium was identical with that of ordinary lead.[4] Furthermore in the same year the experiments of Richards and Lembert,[5] Honigschmidt and Horowitz,[6] and Merton[7] proved the same result. Merton concluded from his 1914 experiments that the difference in wave-length for the λ 4058 line must be less than 0·003 A. Before going on to consider the more recent results it will be as well to discuss the magnitude of the difference to be expected from theory.

109. The magnitude of the Gravitational effect.—In the Bohr theory of spectra the planetary electrons of the atom rotate round the central positively charged nucleus in various

---

[1] *V.* p. 9.

[2] Exner and Haschek, *Sitz. Akad. Wiss. Wien*, iia, **121**, 175, 1912.

[3] *V.* p. 39.

[4] Soddy and Hyman, *Jour. Chem. Soc.*, **105**, 1402, 1914.

[5] Richards and Lembert, *Jour. Amer. Chem. Soc.*, **36**, 1329, 1914.

[6] Honigschmidt and Horowitz, *Sitz. Akad. Wiss. Wien*, iia, **123**, 1914.

[7] Merton, *Proc. Roy. Soc.*, **91A**, 198, 1914.

stable orbits. The frequencies of the spectral lines emitted by the element are associated in an absolutely definite manner with the rotational frequencies of these orbits which are calculated by what is known as a "quantum" relation. Without going further into the theory it will be seen at once that if we alter the force acting between the central nucleus and its planetary electrons these orbits will change and with them the frequency of the light emitted. It is therefore of interest to examine the magnitude of the change, to be expected from this theory, when we alter the mass of the nucleus without changing its charge, and so pass from one isotope to another.

The difference in the system which will first occur to one is that although the electrical force remains the same the gravitational force must be altered. The order of magnitude of the change expected in the total force will clearly be given by considering the ratio between the electrical and gravitational forces acting, to take the simplest case, between the proton and the electron in a neutral hydrogen atom.

Assuming the law of force to be the same in both cases, this ratio is simply e^2/GMm; where e is the electronic charge $4{\cdot}77 \times 10^{-10}$, G the universal gravitational constant $6{\cdot}6 \times 10^{-8}$, M the mass of the proton $1{\cdot}66 \times 10^{-24}$, and m the mass of the electron $9{\cdot}0 \times 10^{-28}$. Putting in these numerical values we obtain the prodigious ratio $2{\cdot}3 \times 10^{39}$. In other words the effect of doubling the mass of the nucleus without altering its charge would give the same percentage increase in the total pull on the planetary electron, as would be produced in the pull between the earth and the moon by a quantity of meteoric dust weighing less than one million millionth of a gramme falling upon the surface of the former body. The gravitational effect may therefore be dismissed as entirely negligible.

110. Deviation of the Bohr orbits due to change in the position of the centre of gravity of the rotating system.—Although we may neglect the gravitational effect there is another, of quite a different order, which arises in the following manner. The mass of the electron compared with that of the nucleus is small but not absolutely negligible, hence it will not rotate about the nucleus as though that were a fixed point, but both will rotate about their common centre of gravity. The position of this centre of gravity will be shifted by any alteration in the mass of the nucleus. If E, M and e, m are the respective charge and mass of the nucleus and the rotating electron, the equation of motion is

$$m \times \frac{r\mathrm{M}}{\mathrm{M} + m} w^2 = \frac{\mathrm{E}e}{r^2}$$

where r is the distance between the two charges and w the angular velocity. Bohr[1] introduced this effect of the mass of the nucleus in order to account for the results obtained by Fowler.[2] The Bohr expression for the frequency then becomes

$$\nu = \frac{2\pi^2 e^2 \mathrm{E}^2 m\mathrm{M}}{h^3 (\mathrm{M} + m)} \left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right)$$

where e, E and m, M are the charges and masses of the electron and nucleus respectively. If we suppose that the atomic weight of lead from radium to be one unit less than that of ordinary lead, this theory predicts a difference in wave-length, for the principle line, of 0·00005 A between the two, a quantity beyond the reach of the most delicate methods of spectrum analysis used up to the present.

111. Later experiments of Aronberg and Merton.—In 1917 Aronberg,[3] applying the extremely high dispersion derived from the spectrum of the sixth order of a Michelson 10-inch grating to the line λ 4058 emitted from a specimen of radio-lead of atomic weight 206·318, observed a difference of 0·0044 Å between this and ordinary lead, of atomic weight 207·20. This remarkable result has been since confirmed by Merton of Oxford[4] who gives the difference of wave-length between radio-lead from pitchblende and ordinary lead as 0·0050±0·0007, Merton made use of a totally different optical system, namely a Fabry and Perot etalon, so that the agreement is very striking.

It is to be noticed that the effect observed was not a mere

---

[1] Bohr, *Nature*, 92, 231, 1913.

[2] Fowler, *Nature*, **92**, 95, 1913.

[3] Aronberg, *Proc. Nat. Acad. Sci.*, **3**, 710, 1917, and *Astrophys, Jour.*, **47**, 96, 1918.

[4] Merton, *Proc. Roy. Soc.*, **96A**, 388, 920.

broadening of the line but a definite shift, and that, though of the same sign, it is about one hundred times greater than that predicted by the Bohr theory. Merton also found a shift of 0·0022±0·0008 Å between the wave-length of thorite-lead and ordinary lead, differing in atomic weight by about 0·6. The heavier atom shows the higher frequency in all cases. This remarkable discrepancy between the shift predicted by theory and that actually observed has been discussed by Harkins and Aronberg.[1]

At a recent discussion on isotopes at the Royal Society[2] Merton commented upon the line 6708 Å emitted by the element lithium, which consists of two components 0·151 Å apart. If lithium is accepted as a mixture of isotopes 6 and 7,[3] he calculated that each of these components should be accompanied by a satellite, some sixteen times as faint, displaced by 0·087 Å. So far he had not been able to observe such satellites. Previous experiments of Merton and Lindemann[4] on the expected doubling in the case of neon had given no conclusive results on account of the physical width of the lines. It was hoped that this difficulty could be overcome by the use of liquid hydrogen temperatures.

Still more recently Merton[5] has repeated his experiments on lead, using a very pure sample of uranium lead from Australian Carnotite. His final results are indicated in the following table :

λ	$\left[\lambda(\text{Carnotite lead}) - \lambda(\text{ordinary lead})\right]$	$\left[\text{Wave number (ordinary lead)} - \text{Wave-number (Carnotite lead)}\right]$
4058	0·011 ±0·0008	0·065±0·005
3740	0·0074±0·0011	0·053±0·008
3684	0·0048±0·0007	0·035±0·005
3640	0·0070±0·0003	0·052±0·002
3573	0·0048±0·0005	0·037±0·004

---

[1] Harkins and Aronberg, *Jour. Am. Chem. Soc.*, **42,** 1328, 1920.

[2] Merton, *Proc. Roy. Soc.*, **99A,** 87, 1921.

[3] *V.* p. 86.

[4] Lindemann, *ibid.*

[5] Merton, *Roy. Soc. Proc.*, **100A,** 84, 1921.

It will be noticed that the shift for the line λ 4058 is rather more than twice that obtained before. Merton suggests that the most probable explanation of this difference is evidently that the Carnotite lead used is a purer sample of uranium lead than that obtained from the pitchblende residues. It is also apparent that the differences are not the same for different lines, an interesting and somewhat surprising result.

112. "Isotope" effect on the Infra-red spectrum of molecules.—The extreme smallness of the isotope "shift" described above in the case of line spectra emitted by atoms is due to the fact that one of the particles concerned in the vibration is the electron itself, whose mass is minute compared with that of the nucleus. Very much larger effects should be expected for any vibration in which two atoms or nuclei are concerned, instead of one atom and an electron. Such a vibration would be in the infra-red region of the spectrum.

This effect was first observed by Imes[1] when mapping the fine structure of the infra-red absorption bands of the halogen acids. In the case of the HCl "Harmonic" band at 1·76μ, mapped with a 20,000 line grating, the maxima were noticed to be attended by satellites. Imes remarks : "The apparent tendency of some of the maxima to resolve into doublets in the case of the HCl harmonic may be due to errors of observation, but it seems significant that the small secondary maxima are all on the long-wave side of the principal maxima they accompany. It is, of course, possible that still higher dispersion applied to the problem may show even the present curves to be composite."

Loomis[2] pointed out that these satellites could be attributed to the recently discovered isotopes of chlorine. In a later paper[3] he has shown that, if m_1 is the mass of the hydrogen nucleus, and m_2 the mass of the charged halogen atom, the difference should be expressed by the quanity $\frac{m_1 m_2}{m_1 + m_2}$ the square root of which occurs in the denominator of the expression

---

[1] Imes, *Astrophysical Journal*, **50**, 251, 1919.
[2] Loomis, *Nature*, Oct. 7, 179, 1920.
[3] Loomis, *Astrophysical Journal*, **52**, 248, 1920.

for frequency. "Consequently the net difference between the spectra of isotopes will be that the wave-lengths of lines in the spectrum of the heavier isotope will be longer than the corresponding lines for the lighter isotope in the ratio $1 + 1/1330 : 1$ for chlorine and $1 + 1/6478 : 1$ for bromine. Since the average atomic weight of chlorine is 35·46 the amounts of Cl^{35} and Cl^{37} present in ordinary chlorine must be as 1·54 : 0·46 or as 3·35 : 1 and, if the lines were absolutely sharp and perfectly resolved, the absorption spectrum of ordinary HCl should consist of pairs of lines separated by 1/1330 of their frequency and the one of shorter wave-length should have about 3·35 the intensity of the other. The average atomic weight of bromine is 79·92, hence the two isotopes are present in nearly equal proportions and the absorption spectrum of HBr should consist of lines of nearly equal intensity separated by 1/6478 of their frequency."

The latter will be too close to be observed with the dispersion employed. In the case of the HCl band at 1·76 μ the difference of wave number on this view should be 4·3. The mean difference of wave number given by Loomis' measurements of 13 lines on Imes' original curves for this band is $4{\cdot}5 \pm 0{\cdot}4$ corresponding to 14 Å in wave-length.

The spectroscopic confirmation of the isotopes of chlorine has also been discussed by Kratzer,[1] who considers that the oscillation-rotation bands of hydrogen chloride due to Imes[2] are in complete accordance with the theory.

[1] H. Kratzer, *Zeit. Physik.*, **3**, 60, 1920.

[2] *Loc. cit.*

CHAPTER XI

THE SEPARATION OF ISOTOPES

113. The Separation of Isotopes.—The importance, from purely practical and technical points of view, of the theory of isotopes would have been insignificant had its application been confined to the radioactive elements and their products, which are only present in infinitesimal quantities on the Earth. But now that the isotopic nature of many elements in everyday use has been demonstrated, the possibility of their separation, to any reasonable extent, raises questions of the most profound importance to applied science. In physics all constants involving, e.g., the density of mercury or the atomic weight of silver may have to be redefined, while in chemistry the most wholesale reconstruction may be necessary for that part of the science the numerical foundations of which have hitherto rested securely upon the constancy of atomic weights.

It is therefore of great interest to consider in turn the various methods of separation proposed and examine how far they have been successful in practice.

114. Separation by Diffusion.—The subject of the separation of a mixture of two gases by the method of Atmolysis or Diffusion has been thoroughly investigated by the late Lord Rayleigh.[1] The diffusion is supposed to take place through porous material. The conditions under which maximum separation is to be obtained are that "mixing" is perfect, so that there can be no accumulation of the less diffusible gas at the surface of the porous material, and that the apertures in the material through which the gases must

---

[1] Rayleigh, *Phil. Mag.*, **42**, 493, 1896.

pass are very small compared with the mean free path of the molecules. If these conditions are satisfied he obtains as an expression for the effect of a single operation :—

$$\frac{x+y}{\mathrm{X}+\mathrm{Y}} = \frac{\mathrm{X}}{\mathrm{X}+\mathrm{Y}} r^{\frac{\nu}{\nu-\mu}} + \frac{\mathrm{Y}}{\mathrm{X}+\mathrm{Y}} r^{\frac{\mu}{\nu-\mu}}$$

where (X Y) (x, y) are the initial and final volumes of the gases, μ, ν, the velocities of diffusion, and r the enrichment of the residue as regards the second constituent.

The velocity of diffusion of a gas is proportional to the square root of the mass of its molecules, so that if a mixture of two isotopes is allowed to diffuse a change in composition *must* be brought about. Now no known isotopes differ from each other much in mass, so the difference between their rates of diffusion will also be small, hence the above equation may be written in the approximate form—

$\frac{x+y}{\mathrm{X}+\mathrm{Y}} = r^{\frac{1}{k}}$ where $k = \frac{\nu-\mu}{\mu}$ a small quantity and,

and, finally, the enrichment by diffusion of the residue as regards the heavier constituent may be expressed with sufficient accuracy by the expression

$$r = \sqrt[\frac{m_2+m_1}{m_2-m}]{\frac{\text{Initial volume}}{\text{Final volume}}}$$

where m_1, m_2 are the molecular masses of the lighter and heavier isotope respectively. In the most favourable case known at present, that of the isotopes of neon, the number over the root is 21 so that the change in composition obtainable in a single operation will in practice be very small.

If we take the density of the original mixture as unity, the increase in density of the residual gas to be expected from the operation of diffusion will be approximately

$$(r-1) \times \frac{\mathrm{Y}}{\mathrm{X}} \times 2\,\frac{m_2 - m_1}{m_2 + m_1}$$

Now neon consists of monatomic molecules differing between each other in mass by 10 per cent. and the heavier is present to the extent of 10 per cent. In the diffusion experiments described on p. 39 the effective ratio of the initial volume to the final volume was estimated as certainly greater than 500 and probably less than 10,000, so that r lies between 1·3 and 1·5. Hence the increase of density of the heavier residue should have been between ·003 and ·005. It was actually ·004.

115. The separation of the isotopes of chlorine by the diffusion of HCl.—In the case of other isotopic gaseous mixtures the numerical obstacles in the way of practical separation will be correspondingly greater. Thus in the case of HCl the 36th root is involved, and in that of HBr the 80th root. The only way by which measurable increase in density may be hoped for will clearly be by increasing the effective ratio of the initial to final volumes to an heroic degree. This can be done by experiments on a huge scale or by a vast number of mechanical repetitions.

Harkins started to attack the HCl problem in 1916 [1] using the first of these two alternatives. In 1920 he mentions a quantity of 19,000 litres of HCl as having been dealt with in these experiments.[2] In the following year [3] he published numerical results indicating that a change in atomic weight of 0·055 of a unit had been achieved.

At the recent discussion on isotopes [4] Sir J. J. Thomson pointed out that a change in the molecular weight of HCl should be caused by allowing a stream of the gas to flow over the surface of a material which absorbed it. The higher diffusion coefficient of the lighter isotope would result in it being absorbed more rapidly than the heavier one, so that the residue of unabsorbed gas should give a higher molecular weight. This "free diffusion" without the interposition of porous material has been recently tried in the Cavendish Laboratory by E. B. Ludlam, but no measurable difference has so far been detected.

116. Separation by Thermal Diffusion.—It has been

---

[1] Harkins, *Jour. Amer. Chem. Soc.*, Feb., 1916.

[2] Harkins, *Science*, Mar. 19, 1920; *Nature*, Apl. 22, 1920; see also *Phys. Rev.*, **15**, 74, 1920; *Science*, **51**, 289, 1920; *Jour. Amer. Chem. Soc.*, **42**, 1328, 1920.

[3] Harkins, *Science*, Oct. 14, 1921; *Nature*, Oct. 3, 1921.

[4] J. J. Thomson, *Proc. Roy. Soc.*, **99A**, 98, 1921.

shown on theoretical grounds independently by Enskog[1] and Chapman[2] that if a mixture of two gases of different molecular weights is allowed to diffuse freely, in a vessel of which the ends are maintained at two different temperatures T,T′, until equilibrium conditions are reached, there will be a slight excess of the heavier gas at the cold end, and of the lighter gas at the hot end. The separation attained depends on the law of force between the molecules and is a maximum if they behave as elastic spheres. The effect was experimentally verified for a mixture of CO_2 and H_2 by Chapman and Dootson,[3] and recently Ibbs[4] has demonstrated that the separation can be carried out continuously and that the time for equilibrium to be established is quite short.

Chapman has suggested[5] that thermal diffusion might be used to separate isotopes. He shows that the separating power depends on a constant k_T. And when the difference between the molecular masses m_1, m_2 is small the value of this is approximately given by

$$k_T = \frac{17}{3} \frac{m_2 - m_1}{m_2 + m_1} \frac{\lambda_1\lambda_2}{9{\cdot}15 - 8{\cdot}25\,\lambda_1\lambda_2}$$

where λ_1, λ_2 denote the proportions by volume of each gas in the mixture; thus $\lambda_1 + \lambda_2 = 1$. The actual separation is given by

$$\lambda_1 - \lambda'_1 = -(\lambda_1 - \lambda'_2) = k_T \log T'/T.$$

He gives the following numerical example: " Suppose that it is desired to separate a mixture of equal parts of Ne^{20} and Ne^{22}, then, writing $m_1 = 20$, $m_2 = 22$, $\lambda_1 = \lambda_2 = \frac{1}{2}$, we find that $k_T = 0{\cdot}0095$. Suppose that the mixture is placed in a vessel consisting of two bulbs joined by a tube, and one bulb is maintained at 80° absolute by liquid air, while the other is heated to 800° absolute (or 527° C.). When the steady state has been attained the difference of relative concentration between the two bulbs is given by the equation

---

[1] Enskog, *Phys. Zeit.*, **12,** 538, 1911; *Ann. d. Phys.*, **38,** 750, 1912.

[2] Chapman, *Phil. Trans.*, **217A,** 115, 1916; *Phil. Mag.*, **34,** 146, 1917.

[3] Chapman and Dootson, *Phil. Mag.*, **34,** 248, 1917.

[4] Ibbs, *Proc. Roy. Soc.*, **99A,** 385, 1921.

[5] Chapman, *Phil. Mag.*, **38,** 182, 1919.

$$\lambda_1 - \lambda'_1 = -(\lambda_2 - \lambda'_2) = 0{\cdot}0095 \log_e 800/80$$
$$= 0{\cdot}022$$

or 2·2 per cent. Thus the cold bulb would contain 48·9 per cent. Ne^{20} to 51·1 per cent. Ne^{22}, and vice versa in the hot bulb. By drawing off the contents of each bulb separately, and by repeating the process with each portion of the gas, the difference of relative concentrations can be much increased. But as the proportions of the two gases become more unequal, the separation effected at each operation slowly decreases. For instance, when the proportions are as 3 : 1, the variation at each operation falls to 1·8 per cent.; while if they are as 10 : 1 the value is 1·2 per cent. This assumes that the molecules behave like elastic spheres: if they behave like point centres of force varying as the inverse nth power of the distance, the separation is rather less; e.g., if $n = 9$, it is just over half the above quantities."

Chapman points out that for equal values of log p/p and log T/T pressure diffusion (centrifuging) is about three times as powerful as thermal diffusion but suggests that it may be more convenient to maintain large differences of temperature than of pressure.

117. Separation by Gravitation or "Pressure Diffusion."—When a heterogeneous fluid is subjected to a gravitational field its heavier particles tend to concentrate in the direction of the field, and if there is no mixing to counteract this a certain amount of separation must take place. If therefore we have a mixture of isotopes in a gaseous or liquid state partial separation should be possible by gravity or centrifuging.

The simplest case to consider is that of the isotopes of neon in the atmosphere and, before the matter had been settled by the mass-spectrograph, analysis of the neon in the air at very great heights was suggested as a possible means of proving its isotopic constitution.[1] The reasoning is as follows:—

If M be the atomic weight, g the gravitational constant, p the pressure, and ρ the density, then if no mixing takes place $dp = -g\rho dh$, h being the height. In the isothermal

---

[1] Lindemann and Aston, *Phil. Mag.*, **37**, 530, 1919.

layer convection is small. If it is small compared with diffusion the gases will separate to a certain extent. Since T is constant

$$p = \frac{\mathrm{RT}\rho}{\mathrm{M}} \text{ and } \frac{d\rho}{\rho} = \frac{\mathrm{M}\rho}{\mathrm{RT}}dh,$$

whence $$\rho = \rho_0 e^{-\frac{\mathrm{M}g}{\mathrm{RT}}\Delta\mathrm{H}},$$

ρ_0 being the density at the height h_0 at which mixing by convection ceases, about 10 kilometres, and Δh the height above this level. If two isotopes are present in the ratio 1 to K_0, so that the density of one is ρ_0 and of the other $\mathrm{K}_0\rho_0$ at height h_0, then their relative density at height $h_0 + \Delta h$ is given by

$$\mathrm{K} = \mathrm{K}_0 e^{-\frac{g\Delta h}{\mathrm{RT}}(\mathrm{M}_1 - \mathrm{M}_2)}.$$

Putting T = 220 as is approximately true in England,

$$\frac{\mathrm{K}}{\mathrm{K}_0} = e^{-5{\cdot}38 \times 10^{-3}\Delta h(\mathrm{M}_1 - \mathrm{M}_2)},$$

Δh being measured in kilometres. If $\mathrm{M}_1 - \mathrm{M}_2 = 2$, therefore

$$\frac{\mathrm{K}}{\mathrm{K}_0} = e^{-1{\cdot}075 \times 10^{-2}\Delta h},$$

It might be possible to design a balloon which would rise to 100,000 feet and there fill itself with air. In this case the relative quantity of the heavier constituent would be reduced from 10 per cent. to about 8·15, so that the atomic weight of neon from this height should be 20·163 instead of 20·2. If one could get air from 200,000 feet, e.g. by means of a long-range gun firing vertically upwards, the atomic weight of the neon should be 20·12.

A more practicable method is to make use of the enormous gravitational fields produced by a high speed centrifuge.

In this case the same equation holds as above except that g varies from the centre to the edge. In a gas therefore

$$\frac{d\rho}{\rho} = -\frac{\mathrm{M}v^2}{\mathrm{RT}} \cdot \frac{dr}{r} = -\frac{\mathrm{M}\omega^2}{\mathrm{RT}}rdr,$$

whence $$\rho = \rho_0 e^{-\frac{\mathrm{M}v_0^2}{2\mathrm{RT}}},$$

v_0 being the peripheral velocity. Here again, if K_0 is the ratio of the quantities present at the centre, the ratio at the edge will be

$$K_0 e^{-\frac{v^2}{2RT}(M_1-M_2)}.$$

A peripheral velocity of 10^5 cm./s. or perhaps even $1{\cdot}3 \times 10^5$ cm./s. might probably be attained in a specially designed centrifuge, so that $\frac{K}{K_0}$ might be made as great as $e^{-0{\cdot}205(M_1-M_2)}$ or even $e^{-0{\cdot}37(M_1-M_2)}$.

If $M_1 - M_2$ is taken as 2 a single operation would therefore give fractions with a change of K of 0·65. In the case of neon the apparent atomic weight of gas from the edge would be about 0·65 per cent. greater than that of gas from the centre, i.e. a separation as great as the best yet achieved in practice by any method could be achieved in one operation. By centrifuging several times or by operating at a lower temperature the enrichment might be increased exponentially.

Centrifuging a liquid, e.g. liquid lead, would not appear so favourable, though it is difficult to form an accurate idea of the quantities without a knowledge of the equation of state. If compression is neglected and the one lead treated as a solution in the other, a similar formula to that given above holds. On assumptions similar to these Poole[1] has calculated that a centrifuge working with a peripheral velocity of about 10^4 cm./sec should separate the isotopes of mercury to an extent corresponding to a change of density of 0·000015.

The only experiments on the separation of isotopes by the use of a centrifuge, so far described, are those of Joly and Poole[2] who attempted to separate the hypothetical isotopic constituents of ordinary lead by this means. No positive results were obtained and the check experiments made with definite alloys of lighter metals with lead were by no means encouraging.

118. Separation by Chemical Action or Ordinary Fractional Distillation.—The possibility of separating isotopes by means of the difference between their chemical affinities or vapour pressures has been investigated very fully

---

[1] Poole, *Phil. Mag.*, **41,** 818, 1921.

[2] Joly and Poole, *Phil. Mag.*, **39,** 372, 1920.

from the theoretical standpoint by Lindemann. The thermodynamical considerations involved are the same in both cases. The reader is referred to the original papers[1] for the details of the reasoning by which the following conclusion is reached :—

"Isotopes must in principle be separable both by fractionation and by chemical means. The amount of separation to be expected depends upon the way the chemical constant is calculated and upon whether 'Nullpunktsenergie' is assumed. At temperatures large compared with $\beta\nu$,[2] which are the only practicable temperatures as far as lead is concerned, the difference of the vapour pressure and the constant of the law of mass action may be expanded in powers of $\frac{\beta\nu}{T}$. The most important term of the type $\log \frac{\beta\nu}{T}$ is cancelled by the chemical constant if this is calculated by what seems the only reasonable way. The next term in $\frac{\beta\nu}{T}$ is cancelled by the 'Nullpunktsenergie' if this exists. All that remains are terms containing the higher powers of $\frac{\beta\nu}{T}$. In practice therefore fractionation does not appear to hold out prospects of success unless one of the above assumptions is wrong. If the first is wrong a difference of as much as 3 per cent. should occur at 1200 and a difference of electromotive force of one millivolt might be expected. Negative results would seem to indicate that both assumptions are right."

As regards experimental evidence it has already been pointed out that the most careful chemical analysis, assisted by radioactive methods of extraordinary delicacy, was unable to achieve the slightest separation of the radioactive isotopes. The laborious efforts to separate the isotopes of neon by a difference of vapour pressure over charcoal cooled in liquid air also gave a completely negative result.

119. Separation by evaporation at very low pressure.—If a liquid consisting of isotopes of different mass is allowed

---

[1] Lindemann, *Phil. Mag.*, **37**, 523, 1919; **38**, 173, 1919.

[2] $\beta\nu$ is the "characteristic" and T the "Absolute" temperature.

to evaporate it can be shown that the number of light atoms escaping from the surface in a given time will be greater than the number of heavier atoms in inverse proportion to the square roots of their weights. If the pressure above the surface is kept so low that none of these atoms return the concentration of the heavier atoms in the residue will steadily increase. This method has been used for the separation of isotopes by Bronsted and Hevesy, who applied it first to the element mercury.

The mercury was allowed to evaporate at temperatures from 40° to 60° C. in the highest vacuum attainable. The evaporating and condensing surfaces were only 1 to 2 cms. apart, the latter was cooled in liquid air so that all atoms escaping reached it without collision and there condensed in the solid form.

It will be seen that the liquid surface acts exactly like the porous diaphragm in the diffusion of gases.[1] The diffusion rate of mercury can be obtained approximately from the diffusion rate of lead in mercury [2] and is such that the mean displacement of the mercury molecule in liquid mercury is about 5×10^{-3} cm. sec.$^{-1}$. It follows that if not more than 5×10^{-3} c.cm. per cm.^{2} surface evaporate during one second no disturbing accumulation of the heavier isotope in the surface layer takes place.

The separation was measured by density determination. Mercury is particularly well suited for this and a notable feature of this work was the amazing delicacy with which it could be performed. With a 5 c.cm. pyknometer an accuracy of one part in two millions is claimed. The first figures published[3] were:

Condensed mercury	0·999981
Residual mercury	1·000031

The densities being referred to ordinary mercury as unity.

The later work was on a larger scale.[4] 2700 c.cm. of mercury were employed and fractionated systematically to about

---

[1] *V.* p. 127.

[2] Groh and Hevesy, *Ann. der Phys.*, **63**, 92, 1920.

[3] Bronsted and Hevesy, *Nature*, Sept. 30, 1920.

[4] Bronsted and Hevesy, *Phil. Mag.*, **43**, 31, 1922.

1/100,000 of its original volume in each direction. The final figures were:

Lightest fraction vol. 0·2 c.c. . .	0·99974
Heaviest fraction vol. 0·3 c.c. . .	1·00023

Mercury behaves as though it was a mixture of equal parts of two isotopes with atomic weights 202·0, 199·2 in equal parts or of isotopes 201·3, 199·8 when the former is four times as strong as the latter, and so on.

120. Separation of the isotopes of chlorine by free evaporation.—The same two investigators were able to announce the first separation of the isotopes of chlorine [1] by applying the above method to a solution of HCl in water. This was allowed to evaporate at a temperature of — 50° C. and condense on a surface cooled in liquid air. Starting with 1 litre 8·6 mol. solution of HCl 100 c.c. each of the lightest and heaviest fraction were obtained.

The degree of separation achieved was tested by two different methods. In the first the density of a saturated solution of NaCl made from the distillate and the residue respectively was determined with the following results:—

Density (salt from distillate) = 1·20222
Density (salt from residue) = 1·20235

These figures correspond to a change in atomic weight of 0·024 of a unit.

In the second method exactly equal weights of the isotopic NaCls were taken and each precipitated with accurately the same volume of $AgNO_3$ solution, in slight excess. After precipitation and dilution to 2,000 c.c. the approximate concentration of the filtrate was determined by titration, also the ratio of Ag concentration of the two solutions was measured in a concentration cell. Calculation showed that the difference in atomic weight of the two samples was 0·021 in good agreement with the density result.

121. Separation by Positive Rays.—The only method which seems to offer any hope of separating isotopes completely, and so obtaining pure specimens of the constituents of a com-

---

[1] Bronsted and Hevesy, *Nature*, July 14, 1921.

plex element, is by analysing a beam of positive rays and trapping the particles so sorted out in different vessels. It is therefore worth while inquiring into the quantities obtainable by this means.

Taking the case of neon and using the parabola method of analysis with long parabolic slits as collecting vessels we find that the maximum separation of the parabolas corresponding to masses 20 and 22 (obtained when electric deflexion θ is half the magnetic) is approximately

$$2\frac{1}{\sqrt{2}}\frac{M_1 - M_2}{M_1}\theta = \frac{\theta}{28}.$$

Taking a reasonable value of θ as ·3 the maximum angular width of the beam for complete separation = 0·01. If the canal-ray tube is made in the form of a slit at 45° to axes, i.e. parallel to the curves, the maximum angular length of the beam might be say 5 times as great, which would collect the positive rays contained in a solid angle of ·0005 sq. radian.

The concentration of the discharge at the axis of the positive ray bulb is considerable, and may be roughly estimated to correspond to a uniform distribution of the entire current over a $\frac{1}{4}$ sq. radian. One may probably assume that half the current is carried by the positive rays, and that at least half the positive rays consist of the gases desired. If neon is analysed by this method therefore the total current carried by the positive rays of mass 20 is

$$\cdot 0005 \times 4 \times \tfrac{1}{2} \times \tfrac{1}{2} \times i = \cdot 0005\, i.$$

If i is as large as 5 milliamperes this $= 1{\cdot}5 \times 10^4$ E.S.U.

$$\text{or} \qquad \frac{1{\cdot}5 \times 10^4}{2{\cdot}7 \times 10^{19} \times 4{\cdot}77 \times 10^{-10}} = 1{\cdot}2 \times 10^{-6} \text{ c.c./sec.},$$

i.e. one might obtain about one-tenth of a cubic millimetre of Ne^{20} and 1/100 cubic millimetre of Ne^{22} per 100 seconds run. It is obvious that even if the difficulties of trapping the rays were overcome, the quantities produced, under the most favourable estimates, are hopelessly small.

122. Separation by photochemical methods.—A remarkably beautiful method of separating the isotopes of chlorine has been suggested by Merton and Hartley which depends upon the following photochemical considerations. Light falling on a mixture of chlorine and hydrogen causes these gases to combine to form hydrochloric acid. This must be due to the activation of the atoms of hydrogen or those of chlorine. Supposing it to be the latter it is conceivable that the radiation frequency necessary to activate the atoms of Cl^{35} will not be quite the same as that necessary to activate those of Cl^{37}. Calling these frequencies ν_{35} and ν_{37} respectively it would seem possible, by excluding one of these frequencies entirely from the activating beam, to cause only one type of chlorine to combine and so to produce pure HCI^{35} or HCI^{37}. Now ordinary chlorine contains about three times as much Cl^{35} as Cl^{37} and these isotopes must absorb their own activating radiation selectively. In this gas therefore light of frequency ν_{35} will be absorbed much more rapidly than that of frequency ν_{37}, so that if we allow the activating beam to pass through the right amount of chlorine gas ν_{35} might be completely absorbed but sufficient ν_{37} radiation transmitted to cause reaction. On certain theories of photo-chemistry light containing ν_{37} but no ν_{35} would cause only atoms of Cl^{37} to combine so that a pure preparation of HCl^{37} would result. Pure Cl^{37} made from this product could now be used as a filter for the preparation of pure HCl^{35}, and this in its turn would yield pure Cl^{35} which could then be used as a more efficient filter for the formation of more HCl^{37}.

Had this very elegant scheme been possible in practice it would have resulted in a separation of a very different order to those previously described and the preparation of unlimited quantities of pure isotopes of at least one complex element. There is however little hope of this, for so far the results of experiments on this method have been entirely negative.

123. Other methods of separation and general conclusions.—The following methods have also been suggested. By the electron impact in a discharge tube, in the case of the inert gases, the lighter atoms being more strongly urged towards the anode;[1] by the migration velocity of ions in gelatine; [2] by the action of light on metallic chlorides.[3]

A survey of the separations actually achieved so far shows that from the practical point of view they are very small. In cases where the method can deal with fair quantities of the substance the order of separation is small, while in the case of complete separation (positive rays) the quantities produced are quite insignificant. We can form some idea by considering the quantity
Q = (difference in atomic weight achieved) × (average quantity of two fractions produced in grammes). As regards the first of these factors the highest figure so far was 0·13 obtained by the writer in the original diffusion experiments on neon, but as the quantities produced were only a few milligrams Q is negligibly small. The highest values of Q have been obtained by Bronsted and Hevesy by their evaporation method.[4] It is 0·5 in the case of Hydrochloric Acid, 0·34 in that of Mercury.

When we consider the enormous labour and difficulty of obtaining this result it appears that unless new methods are discovered the constants of chemical combination are not likely to be seriously upset for some considerable time to come.

[1] Skaupy, *Zeitsch. Phys.*, **3**, 289, 460, 1920.
[2] Lindemann, *Proc. Roy. Soc.*, **99A**, 104, 1921.
[3] Renz, *Zeit. Anorg. Chem.*, **116**, 62, 1921.
[4] *V*. p. 134.

APPENDIX I

Table of atomic weights and isotopes of the elements.—The elements are given in order of their atomic numbers. The different periods are indicated by gaps after the inert gases. A curious relation, pointed out by Rydberg, is that the atomic numbers of all the inert gases are given by taking the series $2\ (1^2 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2 + \ .\ .\ .)$ and stopping the summation at any term. This gives the numbers used by Langmuir (p. 95).

The atomic weights given are the International ones except in the cases marked with an asterisk, where the figures are taken from some of the recent determinations given below.

The isotopes where known are given in order of their atomic masses. The proportion of an isotope in a complex element is indicated by the index letters *a*, *b*, *c* . . . in descending order. In the case of isotopes of the radioactive elements 81–92 the roman numeral gives the number of them believed to exist. The nomenclature of some of the rare earths 69–72 is not yet standardised. The names here are those used by Moseley. Some of these elements, though detected by their X-ray spectra, have never been isolated. The elements corresponding to atomic numbers 43, 61, 75, 85, 87 (all odd) have not yet been discovered.

Recent atomic weight determinations.—The following is a list of some of the elements whose atomic weights have been redetermined quite recently, together with references to the papers in which they were published. Where more than one value is given different methods were used :

Fluorine 19·001. Moles and Batuecas, *Jour. Chim. Phys.*, **18**, 353, 1920.

Aluminium 26·963. Richards and Krepelka, *Journ. Am. Chem. Soc.*, **42**, 2221, 1920.

Silicon 28·111. Baxter, Weatherell and Holmes, *ibid.*, **42**, 1194, 1920.

Scandium 45·10. Honigschmid, *Zeit. Electrochem.*, **25**, 93, 1919.

Tin 118·703. Baxter and Starkweather, *Journ. Am. Chem. Soc.*, **42**, 905, 1920.

118·699. Brauner and Krepelka, *ibid.*, **42**, 917, 1920.

Tellurium 127·73, 127·79. Bruylants and Michielsen, *Bull. Acad. Belg.*, **119**, 1919.
Samarium 150·43. Owens, Balke and Kremers, *Journ. Am. Chem. Soc.*, **42**, 515, 1920.
Thulium 169·44, 169·66. James and Stewart, *ibid.*, **42**, 2022, 1920.
Bismuth 209·02. Honigschmid, *Zeit. Electrochem.*, **26**, 403, 1920.
208·9967. Classen and Wey, *Ber.*, **53**, 2267, 1920.
Antimony 121·773. Willard and McAlpine, *Journ. Am. Chem. Soc.*, **43**, 797, 1921.
Lanthanum 138·912. Baxter, Tani and Chapin, *Journ. Am. Chem. Soc.*, **43**, 1085, 1921.
Germanium 72·418. Miller, *Journ. Am. Chem. Soc.*, **43**, 1085, 1921.
Zinc 65·38. Baxter and Hodges, *ibid.*, **43**, 1242, 1921.
Cadmium 112·411. Baxter and Wilson, *ibid.*, **43**, 1230, 1921.

	Element.	Symbol.	Atomic Number.	Atomic Weight.	Number of Isotopes.	Masses of isotopes.
First Period of 2	Hydrogen	H	1	1·008	1	1·008
	Helium	He	2	4·00	1	4
2nd Period of 8	Lithium	Li	3	6·94	2	6^{b} 7^{a}
	Beryllium	Be	4	9·1	1	9
	Boron	B	5	10·9	2	10^{b} 11^{a}
	Carbon	C	6	12·00	1	12
	Nitrogen	N	7	14·008	1	14
	Oxygen	O	8	16·00	1	16
	Fluorine	F	9	19·00	1	19
	Neon	Ne	10	20·20	2	20^{a} 22^{b}
3rd Period of 8	Sodium	Na	11	23·00	1	23
	Magnesium	Mg	12	24·32*	3	24^{a} 25^{b} 26^{c}
	Aluminium	Al	13	26·96*		
	Silicon	Si	14	28·3	2	28^{a} 29^{b} (30)
	Phosphorus	P	15	31·04	1	31
	Sulphur	S	16	32·06	1	32
	Chlorine	Cl	17	35·46	2	35^{a} 37^{b} (39)
	Argon	A	18	39·9	2	36^{b} 40^{a}
4th Period of 18	Potassium	K	19	39·10	2	39^{a} 41^{b}
	Calcium	Ca	20	40·07	(2)	40 (44)
	Scandium	Sc	21	45·1*		
	Titanium	Ti	22	48·1		
	Vanadium	V	23	51·0		
	Chromium	Cr	24	52·0		
	Manganese	Mn	25	54·93		
	Iron	Fe	26	55·84		
	Cobalt	Co	27	58·97		
	Nickel	Ni	28	58·68	2	58^{a} 60^{b}
	Copper	Cu	29	63·57		
	Zinc	Zn	30	65·37	(4)	(64^{a} 66^{b} 68^{c} 70^{d})
	Gallium	Ga	31	70·10		
	Germanium	Ge	32	72·5		
	Arsenic	As	33	74·96	1	75
	Selenium	Se	34	79·2		
	Bromine	Br	35	79·92	2	79^{a} 81^{b}
	Krypton	Kr	36	82·92	6	78^{f} 80^{e} 82^{c} 83^{d} 84^{a} 86^{b}

	Element	Symbol.	Atomic Number.	Atomic Weight.	Number of Isotopes.	Masses of isotopes.
5th Period of 18	Rubidium	Rb	37	85·45	2	85^a 87^b
	Strontium	Sr	38	87·63		
	Yttrium	Y	39	89·33		
	Zirconium	Zr	40	90·6		
	Niobium	Nb	41	93·1		
	Molybdenum	Mo	42	96·0		
	—	—	43	—		
	Ruthenium	Ru	44	101·7		
	Rhodium	Rh	45	102·9		
	Palladium	Pd	46	106·7		
	Silver	Ag	47	107·88		
	Cadmium	Cd	48	112·40		
	Indium	In	49	114·8		
	Tin	Sn	50	118·7		
	Antimony	Sb	51	120·2		
	Tellurium	Te	52	127·5		
	Iodine	I	53	126·92	1	127
	Xenon	X	54	130·2	(7) 5	(128) 129^a (130) 131^c 132^b 134^d 136^e
6th Period of 32	Caesium	Cs	55	132·81	1	133
	Barium	Ba	56	137·37		
	Lanthanum	La	57	139·0		
	Cerium	Ce	58	140·25		
	Praseodymium	Pr	59	140·6		
	Neodymium	Nd	60	144·3		
	—	—	61	—		
	Samarium	Sm	62	150·4		
	Europium	Eu	63	152·0		
	Gadolinium	Gd	64	157·3		
	Terbium	Tb	65	159·2		
	Dysprosium	Ds	66	162·5		
	Holmium	Ho	67	163·5		
	Erbium	Er	68	167·7		
	Thulium	Tu	69	168·5		
	Ytterbium	Yb	70	173·5		
	Lutecuim	Lu	71	175		
	(Keltium)	(Kt)	72			
	Tantalum	Ta	73	181·5		
	Tungsten	W	74	184·0		
	—	—	75	—		
	Osmium	Os	76	190·9		
	Iridium	Ir	77	193·1		
	Platinum	Pt	78	195·2		
	Gold	Au	79	197·2		
	Mercury	Hg	80	200·6	(6)	(197–200) 202 204
	Thallium	Tl	81	204·0	IV	
	Lead	Pb	82	207·2	XI	
	Bismuth	Bi	83	209·0*	V	
	Polonium	Po	84	—	VII	
	—	—	85	—		
	Emanation	Em	86	222·0	III	
7th Period	—	—	87	—		
	Radium	Ra	88	226·0	IV	
	Actinium	Ac	89	—	II	
	Thorium	Th	90	232·15	VI	
	Uranium X	UX	91		II	
	Uranium	Ur	92	238·2	II	

APPENDIX II

The Periodic Table of the Elements.—The atomic numbers are given in bold type, the atomic weights in italics and the isotopes, where known, in ordinary numerals. The roman numerals indicate the chemical groups and the most important associated valencies are given below them. Elements are placed to the left or to the right of the columns according to their chemical properties, those in the same vertical line as each other have strong chemical similarities. The Rare Earth group is surrounded by a thick line. Elements 59–72 have no properties pronounced enough to give them definite places in the table. The properties of the missing elements can be predicted with

PERIODIC TABLE OF

1 H
1·008

Valency 0	I +1	II +2	III +3	IV +4
2 He *4·00* 4	**3** Li *6·94* 6, 7	**4** Be *9·1* 9	**5** B *10·9* 10, 11	**6** C *12·00* 12
10 Ne *20·2* 20, 22	**11** Na *23·00* 23	**12** Mg *24·32* 24, 25, 26	**13** Al *26·96*	**14** Si *28·3* 28, 29
18 A *39·9* 36, 40	**19** K *39·1* 39, 41 **29** Cu *63·57*	**20** Ca *40·07* **30** Zn *65·37*	**21** Sc *45·1* **31** G *70·1*	**22** Ti *48·1* **32** Ge *72·5*
36 Kr *82·92* 78, 80, 82, 83, 84, 86	**37** Rb *85·45* 85, 87 **47** Ag *107·88*	**38** Sr *87·83* **48** Cd *112·40*	**39** Y *89·33* **49** In *114·8*	**40** Zr *90·6* **50** Sn *118·7*
54 Xe *130·2* 129, 131, 132, 134, 136	**55** Cs *132·81* 133	**56** Ba *137·37*	**57** La *139·0*	**58** Ce *140·25*

59 Pr *140·6*	**60**Nd *144·3*	**61**—	**62** Sm *150·4*	**63** Eu *152·0*	**64** Gd *157·3*	**65** Tb *159·2*
66 Ds *162·5*	**67** Ho *163·5*	**68** Ev *1677*	**69** Tu *168·5*	**70** Yb *173·5*	**71** Lu *175*	**72** (Kt)

Valency 0	I +1	II +2	III +3	IV +4
	79 Au *197·2*	**80** Hg *200·6* 197–204	**81** Tl *204·0*	**82** Pb *207·2*
86 Em *222·0*	**87**-	**88** Ra *226·0*	**89** Ac	**90** Th *232·15*

considerable certainty from the positions of their atomic numbers. From the point of view of the construction of the atom the inert gases should mark the end of the periods as they are shown to do in the list of atomic weights in Appendix I, on the other hand it is more usual in chemistry to start with valency 0. From principles of general convenience of arrangement the latter plan is adopted in this table, which is intended to give the maximum amount of chemical information. Hydrogen, which belongs equally well to group I or group VII, is best omitted from the table altogether.

THE ELEMENTS

V —3	VI —2	VII —1	VIII		
7 N *14·01* 14	**8** O *16·00* 16	**9** F *19·00* 19			
15 P *31·04* 31	**16** S *32·06* 32	**17** Cl *35·46* 35, 37			
23 V *51·0* **33** As *74·96* 75	**24** Cr *52·0* **34** Se *79·2*	**25** Mn *54·93* **35** Br *79·92* 79, 81	**26** Fe *55·85*	**27** Co *58·97*	**28** Ni *58·68* 58, 60
41 Nb *93·5* **51** Sb *120·2*	**42** Mo *96·0* **52** Te *127·5*	**43**— **53** I *126·92* 127	**44** Ru *101·7*	**45** Rh *102·9*	**46** Pd *106·7*
73 Ta *181·5* **83** Bi *209·0*	**74** W *184·0* **84** Po	**75**— **85**—	**76** Os *190·9*	**77** Ir *193·1*	**78** Pt *195·2*
91 U X ii	**92** U *238·2*				

APPENDIX III

Recent results obtained by Dempster.—Thanks to a private communication the writer is able to include some further results obtained by Dempster and a diagram of his apparatus for obtaining positive rays from metals. A full account is to appear in the *Physical Review.* Fig. 19 shows the new arrangement of vaporising furnace A and ionising filament C. The analysing apparatus has already been described on p. 31 and the results with

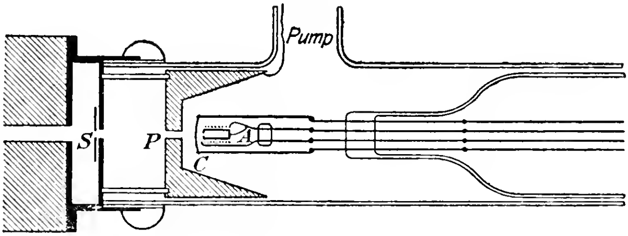


FIG. 19.—Diagram of Anode in Dempster's latest apparatus.

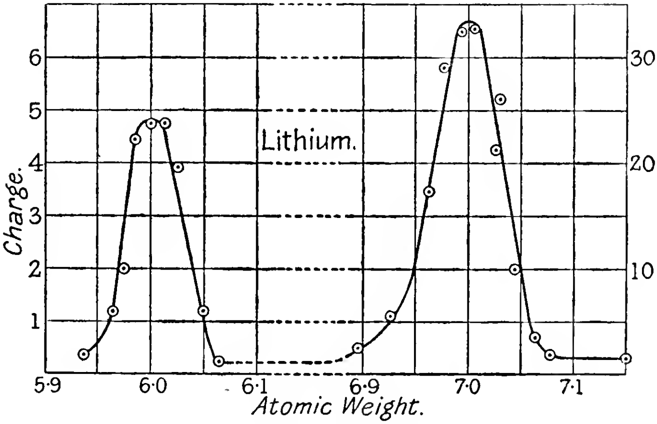


FIG. 20.—Curve for Lithium.

magnesium on p. 81. Fig. 20 shows one of the curves obtained with lithium. It will be seen that the relative intensities of the isotopes is entirely different from that found by the writer (p. 86) and also disagrees very definitely with the chemical atomic weight. Dempster describes these relative intensities as varying very considerably. This is a most remarkable phenomenon and further information upon it is very desirable. There seems just a possibility that the 6 line is enhanced by doubly charged carbon but it is not easy to see where such particles could be produced.

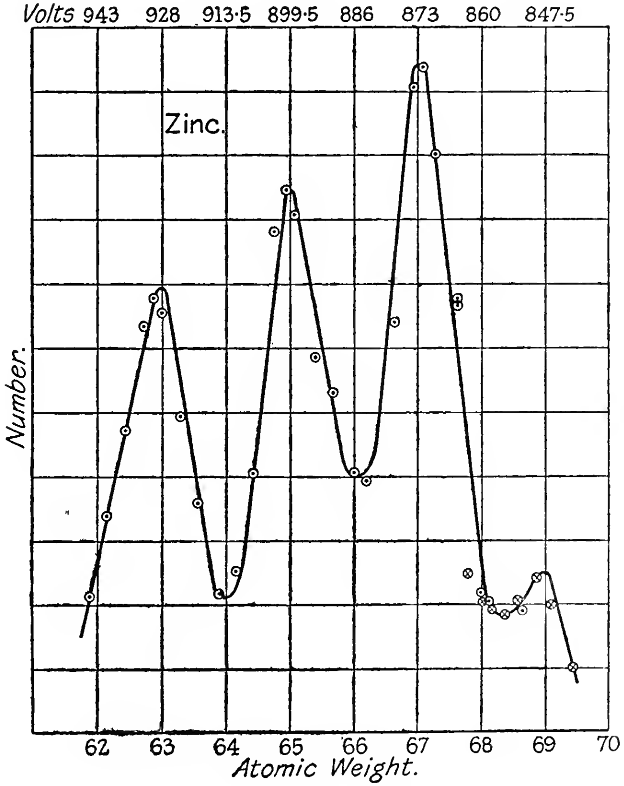


Fig. 21.—Curve for Zinc.

Fig. 21 gives a remarkable curve obtained from zinc. This indicates three strong isotopes and a faint fourth. The absolute scale of atomic weight is not known with certainty, and the values 63, 65, 67, 69 are given by Dempster as those in best agreement with the atomic weight 65·37. Considering that the error in the mean atomic weight of lithium, when calculated on these lines, is about 5 per cent. it would appear possible that these might be a unit too high or too low. The probability of this is strengthened very much by the rule given on p. 110 connecting even atomic number with even atomic weight.

Results with calcium show only one line. This makes it extremely probable that this is a simple element of atomic weight 40 and therefore an isobare of argon.[1]

Note.—In a still later communication Dempster states that he has been successful in using an anode of calcium to which a small quantity of zinc had been added. By this means he is able to compare the masses of the zinc isotopes with the strong calcium maximum, assumed as 40. This gives the atomic weights as 64, 66, 68 and 70. The intensities are quite different to those in the curve given above for zinc. 64 is now the strongest, 66 and 68 fainter, while 70 is very faint indeed. No explanation is yet advanced for these remarkable irregularities in relative intensity.

He has also observed a small maximum at 44 invariably accompanying the strong calcium maximum 40. This he considers to be probably due to an isotope of that element present in small quantity as suggested by the atomic weight 40·07.

The above values are included provisionally in the tables on pages 89 and 142.

---

[1] *V.* p. 88.

INDEX

Printed in Great Britain by Butler & Tanner, *Frome and London.*