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MASS-SPECTRA AND ISOTOPES

BY

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NOB EI LAUREATE

FELLOW OF TRINITY COLLEGE, CAMBRIDGE

This volume incorporates the substance of lectures delivered at the University College of Wales, Aberystwyth, on the Aberystwyth lectures Foundation during the Session 1031—1932.

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PREFACE

It is now nine years since the publication of the second edition of *Isotopes* and the large development of the subject has led me to narrow the scope of the book a little. As the change in the title is intended to indicate, it is now concerned less with general theory and more with experimental results, especially with those obtained by mass-spectrum analysis. In Part III I have attempted to give an account of each individual element relative to its isotopic constitution, a nuclear "chemistry" which so far as I am aware is the first of its kind. The rapid development of artificial transmutation of elements appears likely to create a demand for collected data of this kind in an easily accessible form.

For the contribution of the two chapters on the Isotope Effect in Optical Spectra I am indebted to Dr. C. P. Snow who has made this subject a special study. I have every reason to hope that his treatment of the theory will be welcome to all students of this intricate and rapidly widening field of research.

I wish to thank Professor R. H. Fowler for valuable advice and Dr. K. T. Bainbridge for generous help in connection with the inclusion of his latest work. My thanks are also due to Professors R. T. Birge, A. J. Dempster, F. Soddy and H. C. Urey for providing me with illustrations; to the Council of the Royal Society, the Council of the Chemical Society, Messrs. Macmillan & Co. and Messrs. John Murray for the use of certain plates and figures.

F. W. ASTON.

CAMBRIDGE,
July, 1933.

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MASS-SPECTRA AND ISOTOPES

PART I

HISTORICAL

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 formulae, might show hitherto unsuspected flaws. Such expectations began to be realized 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 generalization, 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 realized 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 1886¹ 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

¹ Crookes, *Nature*, 34, 423, 1886.

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."

Later¹ 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 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

¹ Crookes, *Trans. Chem. Soc.*, 53, 487, 1888 ; 55, 257, 1889.

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 1913² 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* (*loog*, equal, *TOJZOQ*, place) because they occupied the same place in the periodic table of the elements.

5. Progress in the discovery of the non-radioactive elements.—Immediately following the completion of the mass-spectrograph definite proof of the existence of the isotopes of neon was published in November, 1919. A few weeks later the isotopic complexity of chlorine and mercury was demonstrated and the whole number rule formulated, oxygen and carbon being taken as standard simple elements.

Progress in 1920 was rapid. In March the constitution of argon,

¹ V. p. 26.

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.

helium, hydrogen, nitrogen and krypton was published together with a preliminary note on xenon. Boron, fluorine, silicon, bromine, sulphur, phosphorus and arsenic followed in July. Proof of the simple nature of iodine and confirmation of the five principal isotopes of xenon appeared in December, and in the same month Dempster announced his discovery of the isotopes of magnesium.

In February, 1921, the two isotopes of lithium were announced jointly by G. P. Thomson and the writer, and this result was confirmed by Dempster two months later. In the meanwhile the mass-spectrograph had been successfully applied to the anode rays of sodium, potassium, rubidium and caesium, and these analyses were followed by that of nickel in June. In November, G. P. Thomson published results indicating that beryllium was a simple element, and a little later Dempster analysed calcium and zinc.

In June, 1922, largely owing to the valuable properties of schumannized plates, the complexity of tin was demonstrated, and the sixth and seventh isotopes of xenon were confirmed. Results for iron appeared in September and for selenium and aluminium in November. At the same time the probability of the existence of two additional rare isotopes of xenon was indicated. Antimony was analysed a few weeks later.

In 1923 the method of accelerated anode rays was worked out, and resulted in immediate success with many metallic elements. The first analysis of germanium was published in June, and that of copper in August. The analyses of ten more elements : scandium, titanium, vanadium, chromium, manganese, cobalt, gallium, strontium, yttrium and silver were announced at the British Association meeting in Liverpool in September.

In 1924 these results were extended to barium, lanthanum, praseodymium, neodymium, zirconium, cerium, cadmium, tellurium and bismuth. During the next four years attention was turned towards more accurate measurement of mass by means of the second mass-spectrograph ; among the comparatively few new isotopes announced were those of mercury and ordinary lead. Additional isotopes of germanium and sulphur were found.

In 1929, owing to a new means of attack by analysis of the absorption spectra of the air, two rare isotopes of oxygen were announced by Giauque and Johnston. The first mass-spectrum of uranium lead was also obtained. In 1930 chromium, molybdenum and tungsten were attacked successfully by means of their carbonyls and in 1931 osmium, ruthenium, rhenium, thallium and uranium were analysed.

In 1932 the simple constitution of niobium and tantalum was

demonstrated, the hydrogen isotope of mass 2 was discovered and two additional very rare isotopes of mercury.

At the present time out of all the elements known to exist in reasonable quantities only eighteen remain without analysis. Of these eleven are rare earth elements.

CHAPTER II

THE RADIOACTIVE ISOTOPES

6. 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 methods of mass-ray analysis. But progress must then have been exceedingly slow, and the arrival at the real interpretation of the idea, depending as it does on 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 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,³ 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

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

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

³ A. von Welsbach, *Wien. Ber. iia*, 119, 1011, 1910.

shown to be chemically inseparable from radium by Marckwald¹ and Soddy² 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.³

The situation was admirably summed up by Soddy in his report on radioactivity for the year 1910⁴ in the following words :

" These regularities may prove to be the beginning of some embracing generalization, 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 radio-elements, genetic relationships might have resulted in an initial constancy of proportion between the several individuals, which no subsequent 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."

7. 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 appears to have been first entertained by A. S. Russell. With Rossi⁵ 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

¹ Marckwald, *Ber. d. Chem. Ges.*, 40, 3420, 1910.

² Soddy, *Trans. Chem. Soc.*, 99, 72, 1911.

³ Hahn and Meitner, *Physikal. Zeitsch.*, 11, 493, 1910.

⁴ Soddy, *Chem. Soc. Ann. Rep.*, 285, 1910.

⁵ Russell and Rossi, *Proc. Roy. Soc.*, 77A, 478, 1912.

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 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 γ -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 sup-

ported by Soddy¹ but received some adverse criticism on the ground of insufficient evidence. The later work bearing on this point will be described in Chapters XV and XVI.

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 which led to the discovery of the remarkable field of research opened up by the use of radioactive bodies as indicators.⁴ A little later Paneth and Hevesy were able to show the complete identity of the electrochemical properties of Radium D and Lead.⁵

In 1914 Rutherford and Andrade⁶ 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 γ -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.⁷ 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.

8. 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 Soddy⁸ who was the first to suggest, in the form of a valency property, that part of it relating to alpha rays.⁹ 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,¹⁰

¹ Soddy, *Chem. News*, Feb. 28, 1913.

² V. p. 161.

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

⁴ V. p. 17.

⁵ Paneth and Hevesy, *Sitzungber. K. Akad. Wiss. Wien*, **123**, 1037, 1913.

⁶ Rutherford and Andrade, *Phil. Mag.*, **27**, 854, 1914.

⁷ Moseley, *Phil. Mag.*, **26**, 1031, 1913.

⁸ Stewart, *Recent Advances in Physical and Inorganic Chemistry*, Longmans, 1919.

⁹ Soddy, *The Chemistry of the Radio Elements*, 29, First Edition, Longmans, 1911.

¹⁰ Russell, *Chem. News*, Jan. 31, 1913.

but owing to the fact that he failed to realize 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,¹ using as foundation the electrochemical results of Hevesy,² and Soddy, working on the results of a very full chemical investigation carried out at his request by Fleck,³ published the generalization 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 generalization of atomic number discovered by Moseley, 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.

9. 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 Stewart⁴ 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.

10. 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. In the second or β -ray change the particle shot off has a negligible mass and carries a single negative

¹ Fajans, *Physikal. Zeitsch.*, Feb. 15, 1913.

² Hevesy, *Physikal. Zeitsch.*, Jan. 15, 1913.

³ Fleck, *Trans. Chem. Soc.*, 103, 381, 1052, 1913.

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

⁵ V. p. 160.

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, its connection with the velocity with which the rays are ejected together with the intricate researches by which the transformations have been explained belong to the subject of Radioactivity.¹ In connection with the discovery of isotopes it is enough to consider the results now accepted which are indicated in the two diagrams (Figs. 1 and 2).

In the first of these, which is due to Soddy,² the nuclear charge or Atomic number,³ 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 vertical columns edged with thick lines. The atomic weights are shown by fine horizontal lines. All elements lying in the same column will therefore be *isotopes* and all elements lying on the same line 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.

The second diagram 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_1 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 suffers an α -ray change and is 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, 0.04 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

¹ Rutherford, Chadwick and Ellis, *Radiations from Radioactive Substances*.

² Soddy, *The Interpretation of the Atom*.

³ V. p. 161.

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.

There is little doubt that the final product of the actinium series is actinium lead of atomic weight 207.^x Its origin is still somewhat uncertain and it is most probably an isotope of uranium, actino-uranium, of atomic weight 235.

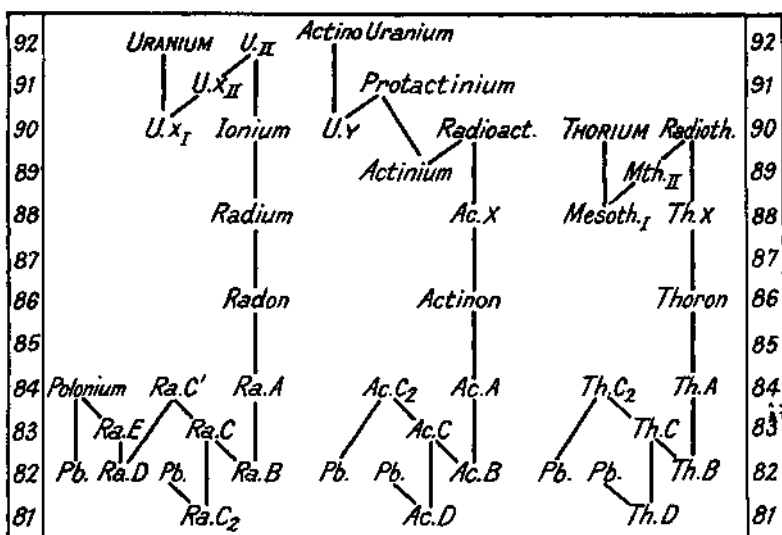


FIG. 2.—Diagram of the radioactive transformations in relation to atomic numbers. In every case a step two downwards is accompanied by the emission of an α -particle and one upwards by a β -particle.

11. 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 radio-activity, 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 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

¹ V. p. 134.

the main thorium chain 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 Soddy¹ 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 Hyman² 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 uranium-lead from Norwegian cleveite gave 206.08,⁵ a very striking agreement with theory. The table of properties on page 17 is taken from his Presidential address to the American Association at Baltimore, December, 1918.

In further confirmation Maurice Curie in Paris⁶ 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 crystallized pitchblende from Morogoro. The high value, 207.9, was also found by Honigschmid for lead from Norwegian thorite.⁷

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 Lambert, *J. Amer. Chem. Soc.*, **36**, 1329, 1914.

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

⁶ M. Curie, *Compt. Rend.*, **158**, 1676, 1914.

⁷ Honigschmid, *Zeit. Elektrochem.*, **24**, **163**, 1918; **25**, **91**, 1919.

	Common Lead.	Mixture Australian.	Uranio- Lead.	Perce Diffe	
	A	B		A · B	ntage rence. A · C
Atomic weight	207.19	206.34	206.08	0.42	0.54
	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

12. 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 preparation 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.

13. 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 and F. Paneth^{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 ionized, but not for non-ionized, 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 crystallizing out. When active lead nitrate and inactive lead chloride are dissolved in molecular proportion in boiling pyridine, the lead in the lead chloride crystallizing 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 interchange 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 crystallizing 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.²

Isotopes can also be used to determine the velocity of diffusion of molecules among themselves.³ 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,

¹ Hevesy and Paneth, *Zeitsch. für Anorg. Chem.*, 82, 323, 1913 ; Brit. Assoc, 1913 ; *Chem. News*, Oct. 13, 166, 1913.

² G. Hevesy and L. Zechmeister, *Ber.*, **53B**, 410, 1920 ; *Zeitsch. Elektrochem.*, 26, 151, 1920.

³ J. Groh and Hevesy, *Ann. Physik.*, IV, 63, 85, 1920.

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 1.16×10^{-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 diffusion coefficient of lead ions diffusing in aqueous solutions is 0.68, this indicates that the molecular diameter of metallic lead is only a third of that of the ion. The latter is probably hydrated.¹ In the same way the rate of diffusion of molecules among themselves has been measured in solid lead² and in lead chloride.³ By the use of thorium B as an indicator the assimilation of lead from solutions by living plants has been investigated by Hevesy⁴ with interesting results. The assimilated (radioactive) lead can be displaced by the introduction of the plant containing lead into another lead solution, whereby inactive lead atoms now take the place of the radioactive ones. From this it follows that the lead is not combined with carbon within the plant, but that it exists in the form of a dissociable salt which is soluble with difficulty.

With the help of radioactive indicators Paneth has been able to demonstrate the existence of metallic hydrides hitherto sought for without success. It has long been suspected that bismuth like its homologues, arsenic and antimony, should form a gaseous hydride, but the usual analytical tests were not sufficiently sensitive to prove this outright. The formation of this gas was demonstrated in the following way: A magnesium foil activated by thorium C, which is isotopic with bismuth, was dissolved in hydrochloric acid, and the hydrogen thus generated conducted into an emanation electroscope. The activity indicated by the electroscope proved that by this treatment several parts per thousand of the thorium C had been converted into a gaseous compound isotopic with bismuth hydride. In this way a practical knowledge of the best way of preparing the compound as well as an idea of its stability were obtained. With the help of this knowledge, the hydride was successfully made from ordinary bismuth in amounts sufficient to prove its existence by chemical methods. Lead hydride was discovered in a strictly analogous manner by first

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

² Groh and Hevesy, *Ann. Physik.*, IV, 65, 216, 1921.

³ Hevesy, *Zeitsch. f. Physik.*, 2, 148, 1920.

⁴ Hevesy, *Biochem. Jour.*, 17, 439, 1923.

using a radioactive isotope, thorium B, to determine whether it existed and then verifying the result by using ordinary lead.¹

A further application of radioactive indicators has been made to the problem of determining the magnitude of the adsorbing surface of powdered crystals.² For example, if powdered lead sulphate is shaken with a saturated solution of the same salt, the PbSO_4 molecules on the surface of the powder are exchanged with those in the solution at a steady rate. If at the beginning of the experiment, thorium B (in the form of the sulphate) is added to the solution and kinetic equilibrium established, it is possible to determine the ratio between the PbSO_4 molecules of the solution and those of the surface by measuring the decrease in the activity of the solution. Thus the number of molecules in the surface of the PbSO_4 powder can be found. From this it can be calculated whether a known quantity of dyestuff adsorbed on this powder forms a layer one or more molecules thick. The investigations performed up to the present indicate that the layer of dyestuffs adsorbed on powdered crystals such as PbSO_4 , PbCrO_4 and PbCl_2 is at the most only one molecule thick. This result is in good agreement with Langmuir's experiments on gaseous adsorption.

¹ Paneth, *Zeitsch. Electrochem.*, 24, 298, 1918 ; *Ber.*, 51, 1704, 1918 ; *Zeitsch. f. Anorg. Chem.*, 35, 549, 1922.

² Paneth, *Zeitsch. f. Electrochem.*, 28, 113, 1922.

For further information the reader is referred to Paneth's book, *Radio Elements as Indicators*, McGraw Hill, New York, 1928.

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, ionization at low pressure in a strong electric field. Ionization, 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 ionized. 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 ionized. It is immensely more massive than the electron, for 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

¹ Goldstein, *Bert. 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.

potential, with sufficient energy to make its presence detectable.¹ 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 pressures² many of its phenomena are not yet fully explained.

For the purposes of describing positive rays it is not necessary to consider 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 is minimized very accurate and consistent measurements can be obtained. Such measurements have been made under a great variety of conditions by the writer.³ The distribution of electric force in the dark space has also been determined for large plane electrodes.⁴

¹ The term "mass rays" has been suggested by Andrade (*The Structure of the Atom*, p. 83) to cover all swiftly moving particles of matter other than electrons. It therefore includes canalstrahlen, positive rays, anode rays, etc., each of which has a more limited scope.

² Compton and Langmuir, *Reviews of Modern Physics*, 2, 123, 1930; Sir J. J. Thomson and G. P. Thomson, *Conduction of Electricity through Gases*, 3rd ed., vol. 2.

³ Aston, *Proc. Roy. Soc.*, 79A, 80, 1907; Aston and Watson, *ibid.*, 86A, 168, 1912; Aston, *ibid.*, 87A, 428, 437, 1912.

⁴ Aston, *Proc. Roy. Soc.*, 84A, 526, 1911.

In the theories on this subject many points are still obscure, but it seems fairly certain that ionization is going on at all points throughout the dark space, and that it reaches a very high intensity in the negative glow. This ionization 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 ionize by collision, liberate more free electrons which, in their turn, become ionizing agents, so that the intensity of ionization 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.

In addition to cathode ray ionization the positive rays travelling towards the cathode themselves are capable of ionizing the gas, and radiation may also play an important part in the same process. The surface of the cathode will 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 $\times$ 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. All the earlier investigations of the rays were made with screens of powdered willemite, which glows a faint green when struck by them, and as early as 1907 Sir J. J. Thomson made observations on hydrogen and helium rays by this means.¹ Dechend and Hammer² photographed the illuminated screen from the outside, but the real advance in technique was made in 1910 by recording the impact of the rays on a photographic sensitized surface introduced inside the evacuated apparatus. This device was first published by Koenigsberger and Kutschewski.³ It was applied independently by Sir J. J. Thomson to his method of analysis with striking results.⁴

¹ J. J. Thomson, *Phil. Mag.*, 13, 561, 1907.

² Dechend and Hammer, *Proc. Heidelberg. Acad. Sci.*, 21, 12, 1910.

³ Koenigsberger and Kutschewski, *Physikal. Zeitschrift*, 11, 666, 1910.

⁴ J. J. Thomson, *Phil. Mag.*, 21, 225, 1911.

18. Sir J. J. Thomson's " Parabola " ¹ 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 1½ 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 cm. long,

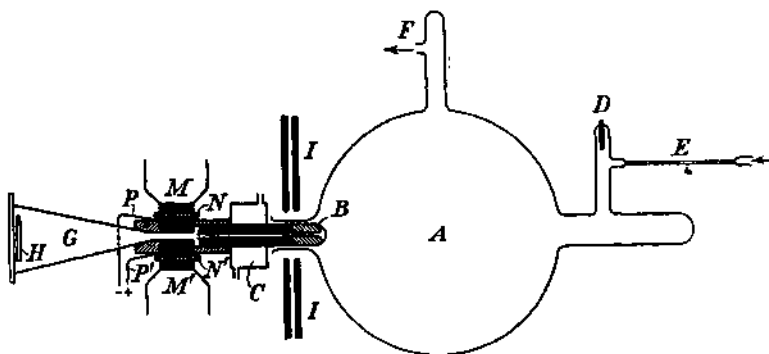


FIG. 3.—Positive Ray Apparatus.

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.

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

¹ For the beautiful modern development of the " parabola " method and its application to chemical problems, the reader is referred to the recent work of Eisenhut and Conrad, *Zeit. f. Electrochemie*, 36, 644, 1930.

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 $x = k(Xe/mv^2)$. 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 $y = k'(He/mv)$, 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 e/m its ratio of mass to charge.

Now e can only exist as the electronic charge 4.77×10^{-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

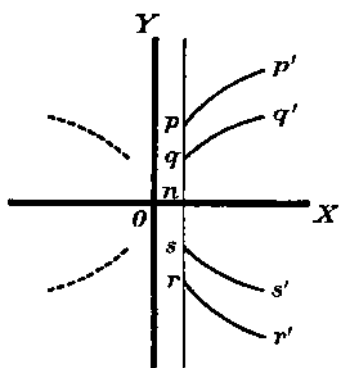


FIG. 4.—Positive Ray Parabolas.

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.

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 ionization 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 recognized 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 ionization in the fine tube the charged particles may easily collide with and capture electrons in passing through it. A 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 ionization 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, written² O^{++} , will be 8. Parabolas due to

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

² In the normal singly-charged ray the plus sign is omitted for convenience.

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 half-way 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 corresponding to normal single charge will 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.

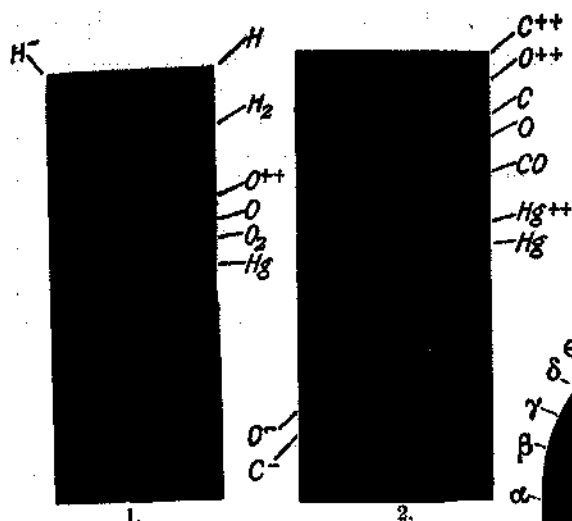
22. Dempster's method of positive ray analysis.—It is clear from the considerations on page 25 that if the positive particles all fell through the same potential and so possessed the same energy, a magnetic field alone would suffice to perform their analysis with regard to mass. A method of analysis based on this idea was 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 $\frac{e}{m} = \frac{2P}{H^2 r^2}$

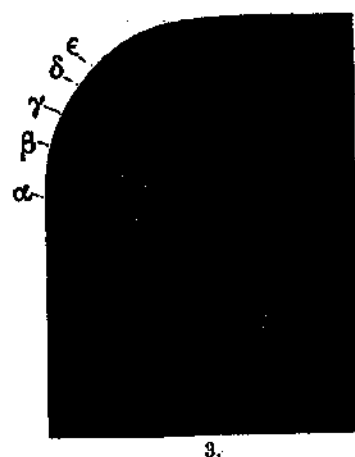
The apparatus consisted of a glass tube G, Fig. 5, where the positive particles fell through a definite potential difference, and the analysing chamber A, in which a strong magnetic field was produced between two semicircular iron plates 2.8 cm. thick and 13 cm. in diameter. The iron plates were soldered 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

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

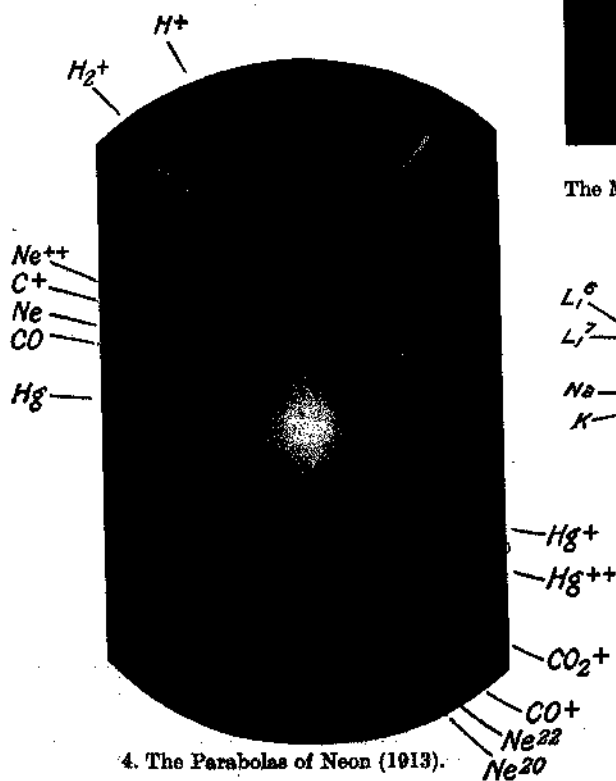
² Classen, *Jahrb. d. Hamburg Wiss. Anst.*, Beiheft, 1907.



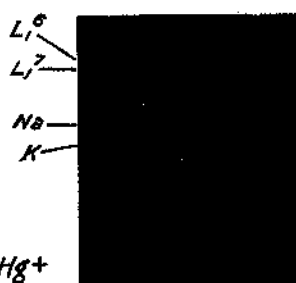
Photographs of Typical Positive Ray Parabolas (1911).



The Multiply Charged Parabolas of Mercury (1912).



4. The Parabolas of Neon (1913).



The Parabolas of Lithium (1921).

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

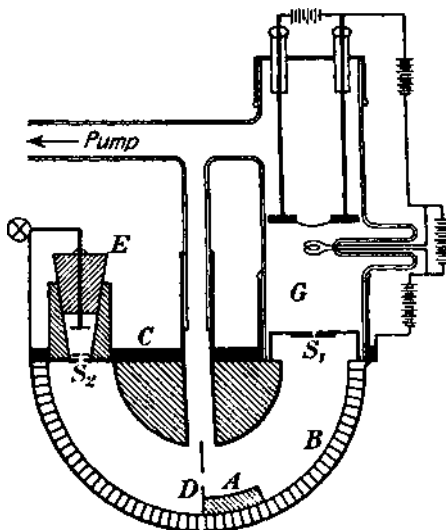


FIG. 5.—Dempster's Apparatus.

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 successful application of this method to the analysis of complex elements will be described in a later chapter.¹

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 Watson¹ and found to correspond with an atomic weight 20.200 ($O = 16$), so that it is the lightest element whose atomic weight differs from a whole number in an unmistakable 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 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

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

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

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 recognized elements which have this molecular weight. Again, if we accept Mendeleeff'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 Mendeleeff'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 Space¹ 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 I (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 radioelements.

These considerations led the author to undertake a searching investigation on the constitution of the gas by two distinct lines of

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

attack, first attempts at separation, secondly examination by positive rays.¹

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. It was therefore necessary to devise some means of determining density accurately, quickly and with the minimum quantity of gas. All these desiderata were obtained by the construction of a simple quartz micro-balance shown in Fig. 6.²

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

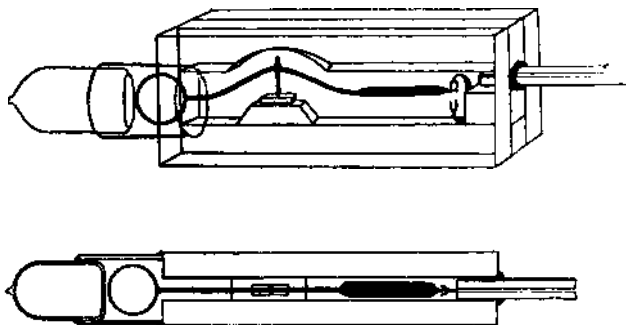


FIG. 6.—Micro-balance.

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

¹ The neon necessary for this research was given by M. Georges Claude of Paris.

² Aston, *Proc. Roy. Soc.*, 89A, 440, 1914.

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 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 00005 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 01 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 :

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 stopcock between it and *a*. After another interval the stopcock was turned, the mercury raised in A and the gas forced into bulb 6. 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 6. 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 6, 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

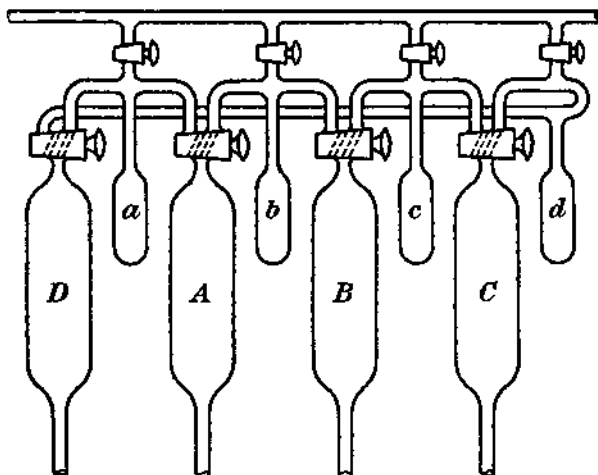


FIG. 7.—Fractionation Apparatus.

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)
12105	120.95	12105	120.90	12100	12105	12105

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 CO₂ 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 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 set-back 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

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

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

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 220. 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 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.²

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

¹ V. p. 27.

² V. p. 220.

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 lead¹ 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 realized 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 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 neon² show beyond any doubt that this gas is a mixture of two isotopes of atomic weights 2000 and 2200 respectively.

¹ V. p. 16.

² Aston, *Phil. Mag.*, 39, 449, 1920.

CHAPTER V

THE FIRST MASS-SPECTROGRAPH¹

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 assum-

¹ The word "mass-spectrograph" was originally intended to be used only for instruments in which the particular sequence of electric and magnetic fields here described is used to give a spectrum depending upon mass alone. As it has been found possible (V. p. 84) to produce photographed mass-spectra by other devices this restriction can no longer logically be insisted upon. For convenience, however, it will be retained in this book.

ing 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 is achieved by the arrangement illustrated diagrammatically in Fig. 8. The exact mathematical analysis has been worked out by R. H. Fowler,² 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

¹ Aston, *Phil. Mag.*, 38, 709, 1919.

² Aston and Fowler, *Phil. Mag.*, 43, 514, 1922.

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.

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

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

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.

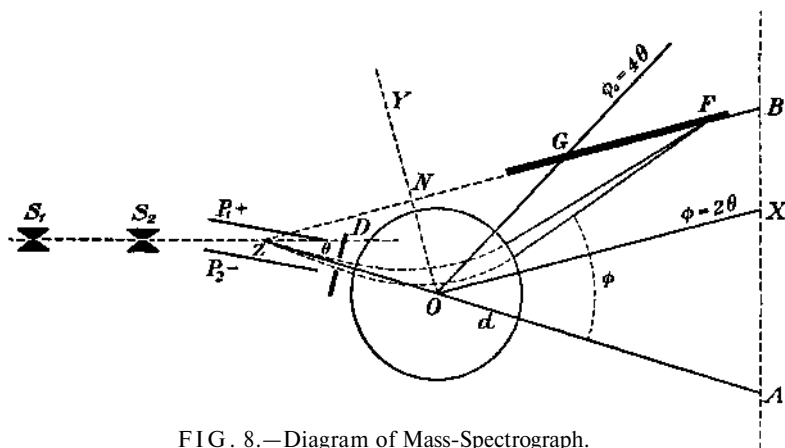


FIG. 8.—Diagram of Mass-Spectrograph.

It follows that over the small range of θ selected by the diaphragm Θv^2 and φv are constant for all rays of given e/m , therefore

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

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 $b\delta\Phi$ at O , and at a further distance r the breadth will be

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

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 $r, 6.2\Theta'$; 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, Θ being here equal to $40'$. 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 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 original 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 surrounded concentrically by an insulated aluminium tube to protect the glass walls, as in the Lodge valve.

The aluminium cathode C, 2.5 cm. wide, is concave, and 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 end of the bulb, which would be immediately melted by the very concentrated beam of cathode rays, a silica bulb *D* 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 was earthed.

The discharge was maintained by means of a large induction-coil actuated by a mercury coal-gas break ; about 100 to 150 watts were

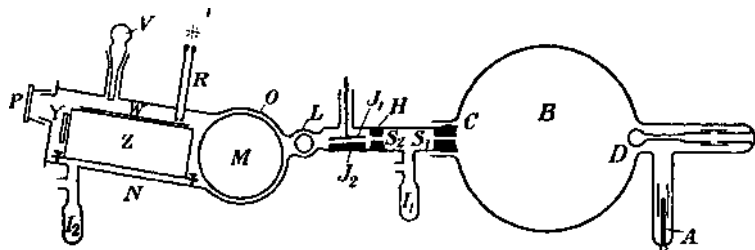


FIG. 9.—Diagram of the First Mass-Spectrograph.

passed through the primary, and the bulb arranged to take from 0.5 to 1 milliamperes 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

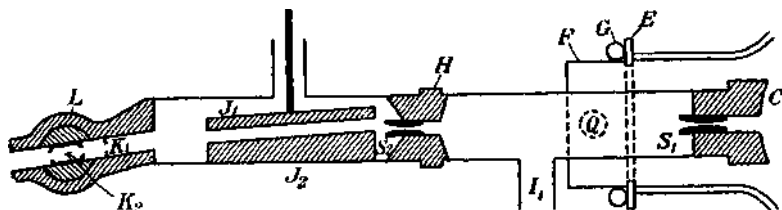


FIG. 10.—Mounting of Cathode of First Mass-Spectrograph.

flat brass collar *E*, which forms the mouth of an annular space between a wide outer tube *P* 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 was kept cool by circulating water through the copper pipe shown in section at *G*.

The gas to be analysed was 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 was performed by a Gaede mercury-pump through a similar tube on the

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



THE ORIGINAL MASS-SPECTROGRAPH SET UP IN THE CAVENDISH LABORATORY IN 1919;
NOW IN THE SCIENCE MUSEUM, SOUTH KENSINGTON.

B, Discharge Tube. *A*, Anode connected to high potential terminal of induction coil below table. *C*, Reservoir containing gas to be analysed. *J*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.

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, this arrangement is far more satisfactory and has the additional advantage of enabling the bulb to be dismantled 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 0.3 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, 0.01 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 position of the two slits is indicated in the diagram. They were roughly 0.05 mm. wide by 2 mm. long and could be accurately adjusted parallel to each other by means of their diffraction patterns. The space between them was exhausted by the liquid-air-cooled charcoal tube I_1 .

37. The Electric Field.—The spreading of the heterogeneous ribbon of rays formed by the slits into an electric spectrum took 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 was earthed. The upper surface was 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 were 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 passed 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 was 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, which is exhausted by the charcoal tube I_2 , 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 passed between two vertical earthed brass plates Z, Z about 3 mm. apart, and finally reached 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 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 x 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 sensitized 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.

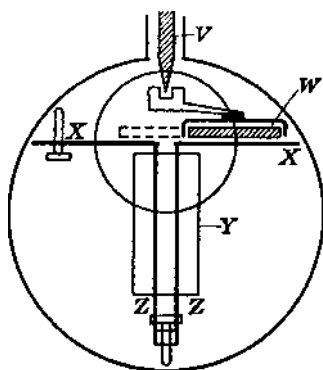


FIG. 11.- The Plateholder of the Camera.

40. Experimental procedure.—The plate having been dried in a high vacuum overnight, the whole apparatus was exhausted as completely as possible by the pump with the stopcock L open. I_1 and I_2 were then cut off from the pump by stopcocks and immersed in liquid air for an hour or so. The electric field, which ranged from 200 to 500 volts, was 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 could be inspected through the plate-glass back of the cap P. In the meantime the leak, pump, and coil, had all been started to get the bulb into the desired state.

When this was steady, J_1 was earthed, to prevent any rays reaching the camera, and the plate moved over the slot to its first position. The magnet current having been set to the particular value desired and the diaphragm adjusted, the coil was momentarily interrupted

and J_1 raised to the desired potential, after which the exposure took place. During this, preferably both at the beginning and the end, light from a lamp T was 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 ranged from 20 seconds in the case of hydrogen lines to 30 minutes or more, 15 minutes being usually enough. As soon as it was complete the above procedure was repeated, and the plate moved into the second position. In this way as many as six spectra could be taken on one plate, after which L was shut, I_2 warmed up, and air admitted to the camera. The cap P, which is on a ground joint, could now be removed, and the exposed plate seized and taken out with a special pair of forceps. A fresh plate was now immediately put in, P replaced and the camera again exhausted, in which state it was left till the next operation.

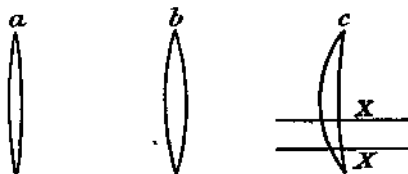


FIG. 12.—Form of the Spectrum Lines.

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 deflecting fields were unaffected by the passage of the rays. This appears to be the case in the magnetic field, but owing to an obscure polarizing effect¹ the electric field is weakened in the region of the beam, allowing rays of smaller energy to pass the diaphragm. As this effect is greatest in the centre this part of the beam will be more deflected by the magnet and the spot will take the form shown at *c*.

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)

¹ V. p. 77.

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 $\tan \frac{1}{2} \phi = d/R$. But X and Θ are constant, hence mv^2 must be constant so that the radius of curvature in the magnetic field varies as m . We may therefore write

$$\tan \frac{1}{2} \phi = (m_0/m) \quad . \quad . \quad . \quad (4)$$

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

$$NF = p \cot (\phi - 20) \quad . \quad . \quad . \quad (5)$$

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 $\tan \frac{1}{2} \phi = \tan 20$. Thus the mass-scale is approximately linear near $\phi = 40$.

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 plate 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 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 $\tan 20$ 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 was a purely empirical process, and consisted 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

¹ Aston and Fowler, *Phil Mag.*, 43, 515, 1922.

² V. p. 46.

as that described below, 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

$$\frac{m'_1}{m_1} = \frac{m'_2}{m_2} = \frac{m'_3}{m_3} = r \text{ where } r \text{ is clearly a measure of the change in } m_0$$

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.

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 $m'/m = X/X' \times (H'/H)^2$. 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, was kept constant and X was assumed to be proportional to the potential applied to the plates P_1, P_2 . Thus the position occupied by the line 12 due to carbon with a potential on the plates of 320 volt³ should be exactly coincident with that occupied by line 16 due to oxygen with 240 volts, when the magnetic field was held constant. All such coincidences were found to occur to the accuracy then attainable.

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. 20, 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 H , 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 out¹ 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 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 of the method of coincidences has been the underlying one in the development of methods of precision. Its first notable application was in the measurements of the masses of helium and hydrogen.

45. The determination of the masses of atoms of hydrogen and helium by the method of "Bracketing."—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

¹ P. 26,

the electric plates first in parallel and then in series, then magnetic field being kept constant, all masses having an exact two to one relation will be brought into coincidence on the plate.¹ 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 H₂. In the same way He was compared with O⁺⁺, and H₃.² The method is discussed on p. 49. The values obtained by its use can be checked in the ordinary way by comparing He with C⁺⁺ and H₃ 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 :

Lino.	Method.	Mass assumed.	Mass deduced.
He	{ Bracket	O ⁺⁺ = 8	3.994-3.996
	{ Direct	C ⁺⁺ = 6	4005-4010
H ₃	{ Bracket	C ⁺⁺ = 6	3025-3027
	{ Direct	Ho = 4	3021-3030
H ₂	Bracket	He = 4	2012-2018

These figures led to the conclusion that hydrogen was a simple element and that the mass of its atom corresponded to the chemical atomic weight and was definitely divergent from a whole number. Incidentally they furnished conclusive proof that the body of mass 3 first observed and investigated by Sir J. J. Thomson³ was actually a molecule consisting of three hydrogen atoms, a result independently established about the same time by the chemical work of Wendt and Landauer.⁴

¹ V. p. 48.

² V. p. 100.

³ J. J. Thomson, *Rays of Positive Electricity*, p. 116, 1913.

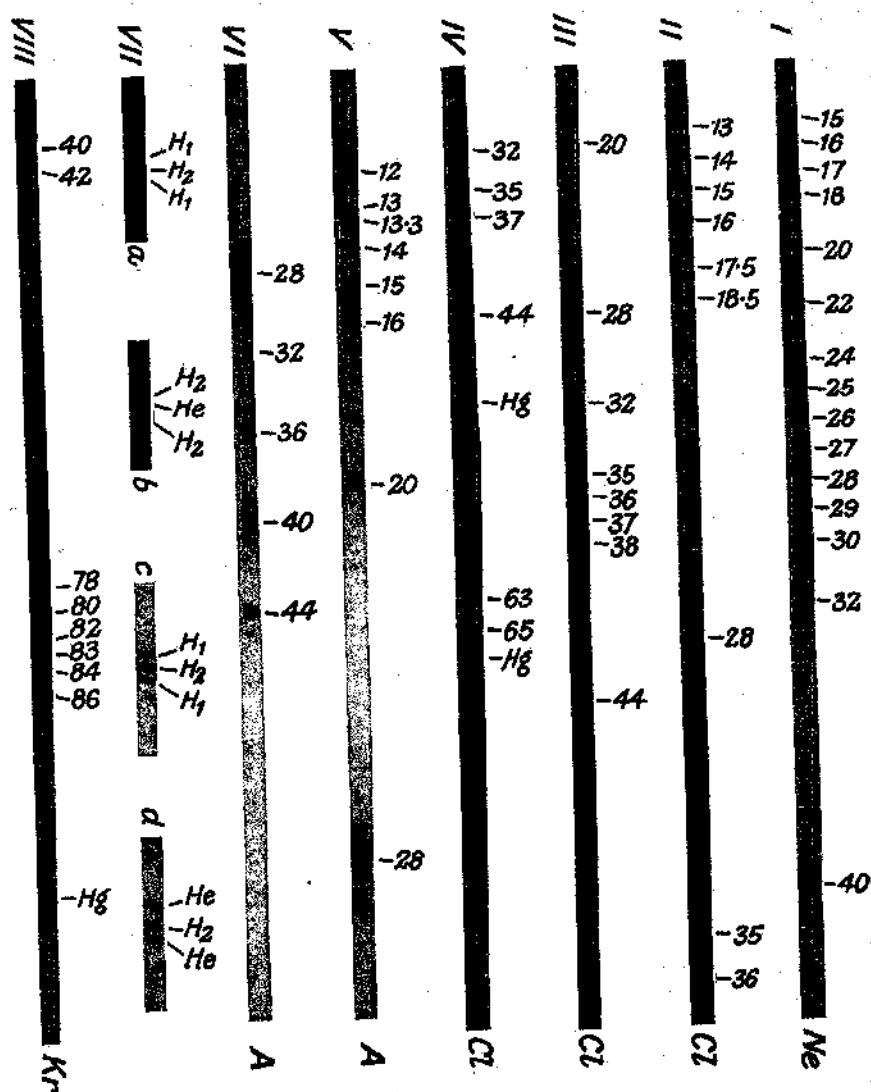
⁴ Wendt and Landauer, *Jour. Amer. Chem. Soc.*, 42, 930, 1920.

46. 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 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 minimized 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.

47. Resolving power and accuracy of mass determination.—Taking the width of the slits as $1/25$ mm. and putting in the dimensions of the apparatus the theory shows that in the region $\phi = 40$ 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 proved 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



TYPICAL MASS-SPECTRA OBTAINED WITH THE FIRST MASS-SPECTROGRAPH, 1920.

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 1000 could 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 was 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 1000 was attainable.

48. Lines of the First, Second and higher Orders.—It was shown on page 27 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.

49. 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, was 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 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

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

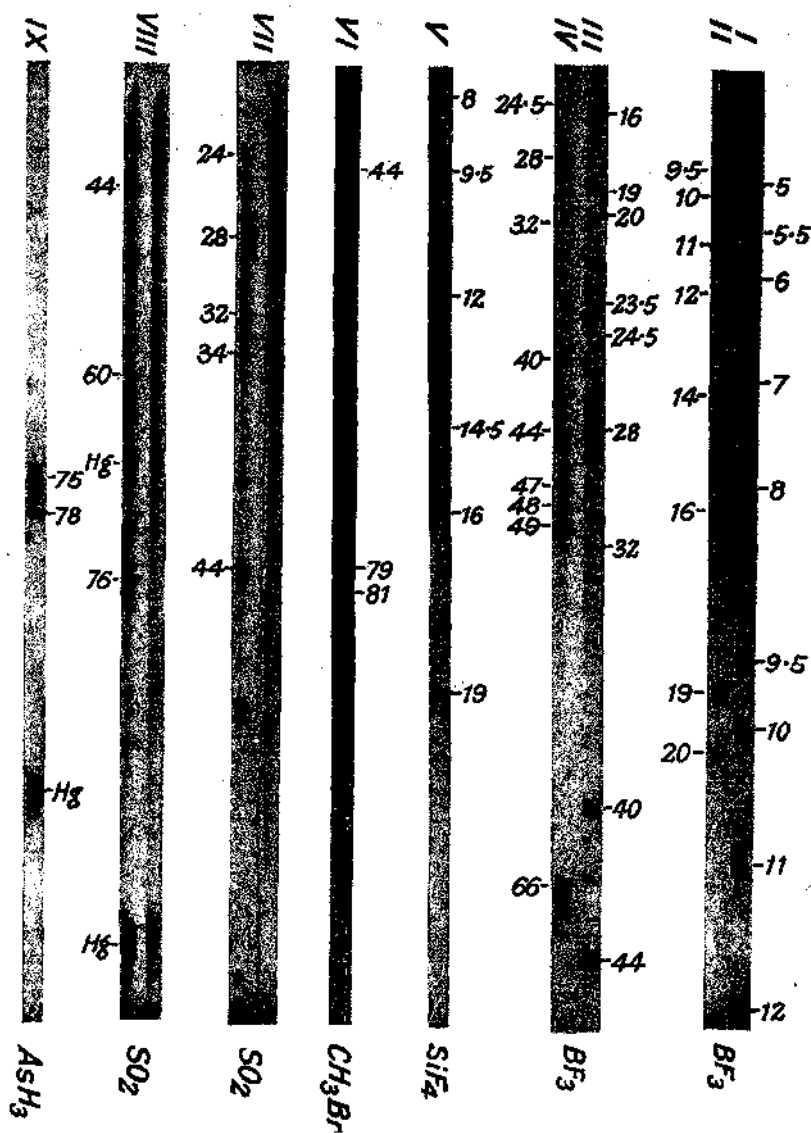
47 and 49 cannot by any reasonable argument be elementary, they must in fact be due to compounds of fluorine.

50. 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.

51. Mass-numbers.—The problem of nomenclature of the isotopes became serious when the complex nature of the heavy elements was proved. The plan generally adopted at present is to use the chemical symbol of the complex element with an index corresponding to its mass : e.g. Ne^{22} , Rb^{87} . This index is called the "mass-number" of the atom. It may be defined in two ways. Theoretically, it is the number of protons in the atom, practically it is the nearest whole number to its weight expressed on the ordinary chemical scale. These integers are identical in all cases so far as our knowledge extends at present.

52. Results obtained with the First Mass-spectrograph.—The original instrument, adapted from time to time to suit particular needs, was in continual use from 1919 till it was dismantled in 1925, with results which will be given in Part III. Typical spectra obtained by its means are reproduced in Plates III and IV. The first experiments were done on neon and the spectra obtained gave the first entirely satisfactory proof that this consisted of isotopes each of whole number mass.¹ As the work progressed with chlorine and other complex elements it soon became clear that all atoms had masses which were integrally related to a close approximation, the "whole number rule." Hydrogen, as theoretically expected, was found to be an exception to this. Indications were obtained that other elements such as lithium and iron would show similar but smaller variations, but the measurement of these required more powerful instruments and methods the development of which will now be described.

¹ Aston, *Phil. Mag.*, 39, 449, 1920.



TYPICAL MASS-SPECTRA OBTAINED WITH THE FIRST MASS-SPECTROGRAPH, 1920.

PART II

PRODUCTION AND ANALYSIS OF MASS-SPECTRA

CHAPTER VI

TECHNIQUE OF GAS DISCHARGE

53. Objects to be Attained.—As in optical spectra, advance in the analysis of mass-spectra is definitely limited by the intensity of the source of rays. It is useless to design apparatus of higher resolving power unless the intensity of illumination of the image-forming slit is increased to correspond. The most convenient and controllable source of intense beams of mass-rays is the discharge in a gas at low pressure. As has already been stated, our knowledge of the mechanism of this is still incomplete and largely empirical. To take advantage of the fact that the slit to be illuminated is usually extremely small it has always been the writer's aim to devise forms of discharge which give beams of rays sharply concentrated rather than of great total intensity. Other things being the same, the latter can always be obtained by forcing more current through the discharge, but beyond a certain point this soon defeats its object by limiting the duration of the exposure and in many other ways.

54. Cylindrical Discharge Tubes.—In all the very early work on canal rays by Goldstein, J. J. Thomson, Wien and others, cylindrical discharge tubes were used, and for many types of research they are undoubtedly the most effective. The concentration of the positive stream towards the centre of the cathode is very marked as the negative glow retreats under reduced pressure. This concentration, which is indicated in Fig. 13, conveniently limits the working area of the cathode so that a gap can be left between it and the walls allowing gas to be introduced or pumped off at cathode (generally earth) potential. At the same time it automatically focusses the beam towards the centre where the slit is placed.

At first sight it would appear that by accurate lining up of the tube and proper reduction of pressure a solid beam of rays of indefinitely high intensity could be focussed on the geometrical centre of the cathode travelling in the direction of the axis of the **tube**. **Unfortunately** in practice it is found that beams focussed in **this way**

resemble hollow cones rather than solid rods, so that with a very fine slit it is the accidental coincidence of this with the edge rather than with the middle of the cone which is effective. Since the position of these areas of high concentration seems to depend on minute alterations of the geometry of the tube and cathode, the element of chance is always present, but once a good setting has been obtained it will usually last for a considerable time. The anode may be located anywhere beyond the dark space. In order to dissipate the energy

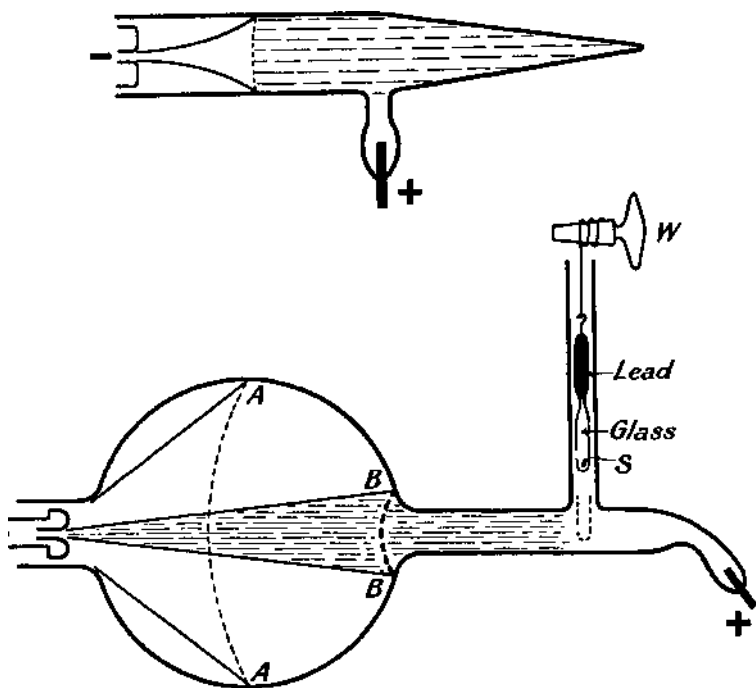


FIG. 13.—Cylindrical and Spherical Discharge Tubes (for the production of mass rays).

of the cathode rays the simplest plan is to draw off the end of the tube into a long taper, as shown in the figure.

55. Spherical Discharge Tubes.—For practically the whole of the writer's work on mass-spectra obtained by gas discharge large spherical "bulb" discharge tubes were employed. The form at present adopted after many years' experience is shown in Fig. 13. The bulb is 8 in. in diameter—6-in. bulbs have also been used—with a neck 1.5 in. internal diameter containing the cathode. This is a solid hemisphere of aluminium 1 in. in diameter drilled with a hole of about 3 millimetres and turned to the toroid section indicated by rounding off the edges. This form, although it is slightly less efficient,

is preferred to the concave type used with the first mass-spectrograph because it appears to be less acutely sensitive to change in position and does not necessitate a special anticathode to dissipate the energy of the cathode rays. These are given off from a cathode of this form in two groups, a diffuse wide cone striking the walls as far back as the circle A, A, and a much more concentrated beam emerging from the cathode pit as the cone B, B, the energy of which is dissipated in the long neck tapered and terminating in the anode as shown. With this arrangement 1 milliampere at 40 kilovolts can be used for an indefinite period without any artificial cooling of the glass walls being required.

The best position for the cathode in the neck is roughly as shown, but has to be found by trial for any fresh setting of the apparatus. The concentration of the beam of mass rays into the cathode pit appears to be produced in a similar manner, but at much lower pressures, to that in the cylindrical form and is extremely sensitive to change in geometry. The shift sideways of the neck with respect to the cathode of a fraction of a millimetre may make all the difference between success and failure so that a good setting cannot always be reproduced after the bulb has been dismounted. On the other hand, once obtained a favourable setting can be used continually until the walls of the neck become coated with aluminium sputtered from the cathode or other products of decomposition. This coating may be cleaned off with weak hydrofluoric acid solution and the bulb used again.

56. Introduction of the sample into the discharge.—In the case of gases or materials having high vapour pressures admission to the discharge is made continuously through a fine glass leak. The rate is controlled by pressure in the reservoir and balanced by pumping to give the desired hardness to the discharge. The inlet and outlet tubes should be behind the cathode where the gas is not at high potential. Compounds such as uranium fluoride or osmium tetroxide having vapour pressures too low for a fine leak may be admitted through a small stopcock either continually, the rate being controlled by temperature adjustment, or in doses. If the boiling-point is too high for this a special vertical winch arrangement must be attached as indicated (Fig. 13). The solid is placed in a glass bucket and lowered by means of the winch W into the anode neck where it is vaporized by the heat of the cathode ray stream. This method has been successfully employed for selenium and rhenium heptoxide.

57. Relative Merits of Cylinders and Bulbs.—This question has been the subject of a good deal of controversy and the answer really depends on the particular class of work for which the rays

are required. The **bulb** type was introduced during the early work on positive rays in the Cavendish Laboratory because it enabled the discharge to pass at the lowest pressures. This was of the first importance at a time when large "canal" tubes were used and no means, or only inadequate means, were available for reducing the pressure in the camera below that of the discharge. Nowadays the use of extremely fine apertures and improved means of maintaining high vacua have removed some of the objections to the higher discharge pressure in cylinders, and Wien claims that these are overwhelmingly superior to bulbs when the total quantity of rays passing through the small aperture at the centre of the cathode is measured. The writer's experience agrees with this as far as total quantity, as opposed to constitution, of the rays is concerned. The bulb is in general inferior to the cylinder in this respect, but if sufficient pains are taken to get the cathode into the best position its inferiority is not nearly so marked as the figures published by Dopel¹ would suggest. The cylindrical tube is easier to make and to fit. It can be exhausted much quicker and is therefore particularly suitable for preliminary testing. It was used in this way in connection with the second mass-spectrograph and proved of the greatest value in providing bright hydrogen lines for visual observation on the willemite screen. On the other hand, the rays produced in a cylindrical discharge tube have their energies concentrated into a very much smaller range than those of a bulb. This, though advantageous in some cases, is entirely unsuitable for measurements of mass of high precision which depend on the comparison of particles with energies differing by a ratio as high as 2 to 1. Furthermore, the low-pressure discharge in the bulb appears to be much more favourable to the formation of those multiply charged particles which are necessary to establish and check accurate ratios of mass.

58. Peculiarities of Gas Discharge.—After over twenty-five years' experience with vacuum discharges the writer knows no method of obtaining, still less of reproducing, first-class results with any certainty. Although our knowledge has advanced enormously in that period² there are still many gaps, and the extreme complexity of the mechanism of this form of discharge renders its use much of an art rather than a science. Both its phenomena and its limitations abound in the curious and unexpected.

There is, for instance, the fact that though it gives highly satisfactory results with potentials of 10 to 60 kilovolts above the latter ever-increasing experimental difficulties develop. The discharge be-

¹ Dopel, *Ann. der. Physik.*, 4, 23, 1925.

² Compton and Langmuir, *Rev. of Modern Phys.*, 2, 123, 1930.

comes impracticable and to obtain positive rays of 100 kilo volts or over, such as are required for artificial disintegration, supplementary high vacuum accelerating fields must be used. Thus in the well-known experiments of Cockcroft and Walton¹ the protons were generated in a cylindrical tube with a toroid cathode at a low voltage and then passed through suitable accelerating fields to raise their energy to the value required. An ingenious method for producing high-speed mass rays without the use of high voltages has been described by Lawrence and Sloan.²

The inert gases must always be diluted with some other gas such as carbon dioxide, otherwise they cause excessive sputtering of the cathode. It may be taken as a general rule that pure materials do not behave well in the gas discharge and tend to make it unsteady. The presence of heavy ions such as mercury usually steady the discharge. It has long been known that the introduction of a heavy inert gas may be beneficial.³ On the other hand, the presence of elements of low ionization potential such as mercury may suppress the production of mass ray of others entirely. Thus all the early attempts to produce the mass-spectrum of zinc from the discharge in zinc methyl failed completely and it was only by using the vapour in the absence of mercury that success was achieved. It is still more mysterious that the corresponding cadmium compound under the same conditions refused to yield any trace of cadmium lines. An excellent example of the extraordinarily uncertain nature of this type of research is afforded by the analysis of rhenium heptoxide.⁴

59. Effects of Compounds in the Discharge.—Looked at purely as a means of discovering and identifying isotopes the gaseous discharge has the defect that it produces a wealth of molecular lines in addition to the atomic ones required, and although in exceptional cases these afford valuable confirmation, in general they merely confuse the evidence and render its interpretation more difficult. In the first place allowance must always be made for the presence of compounds of hydrogen, carbon, oxygen and silicon derived from the walls of the discharge tube. There is little doubt that the faint isotopes of oxygen 17 and 18 would have been discovered on the mass-spectra of that element had there been any means of guaranteeing that effects produced at these positions were not due to OH and OH₂.

In combining with an element to give lines which may be mistaken for its isotopes hydrogen is obviously the only serious culprit. In

¹ Cockcroft and Walton, *Proc. Roy. Soc. A*, **136**, 619, 1932.

² Lawrence and Sloan, *Proc. Nat. Acad. Sci.*, **17**, 64, 1931.

³ Aston, *Proc. Roy. Soc. A*, **103**, 468, 1923.

⁴ V. p. 155.

the early days all faint lines immediately following strong ones were regarded with the greatest suspicion. The lines 33 and 34 (Spectrum VII, Plate IV) were taken to be hydrides of sulphur and another at 21 to be an abnormal hydride of neon. When later it was found that these actually were true isotopes these precautions were relaxed to a certain extent with the unfortunate result that lines 65 and 69 in the mass-spectrum of zinc obtained by the discharge through its methyl were erroneously ascribed to true isotopes. It is particularly unfortunate that the discharge through lead methyl gives traces of hydrides, for this is the only means so far available for obtaining an intense spectrum of lead.¹ This hydride effect seriously reduces the accuracy and reliability of the measurements of abundance of its isotopes which are of such profound importance in connection with the geological time scale.

60. Bands in Mass-spectra.—Attention has already been called to effects produced in the parabola method of analysis by collisions made by the rays in the camera itself and called by Sir J. J. Thomson "secondary rays."² The particular arrangement of opposed fields in the mass-spectrograph virtually prevents effects of this kind by reducing them in general to a faint continuous background on the mass-spectra produced. If, however, very intense molecular beams are in use and the vacuum in the camera is allowed to deteriorate, interesting secondary phenomena may be observed. One of these effects was first noticed while the second mass-spectrograph was in process of construction. On this occasion very wide slits, with resulting poor vacuum in the camera, were being used for testing, and a distinct broad band was observed on the willemite screen in the region corresponding to a mass of half a unit.

Some years later during the preliminary running in of a new discharge bulb, which always results in abnormally strong beams of rays, a similar band effect was noticed on a photographed mass-spectrum, this time in the region 5·2. The matter was further investigated and the band in region 0·5 was again observed and this time photographed. It was found that the positions of the bands on the mass scale were not affected by the alteration of the fields. Fig. 14 shows the photometric observations on the bands which show their centres to be 0·515 and 5·18 respectively. A special subsidiary electric deflecting field was now attached to the camera and by observations with this it was demonstrated beyond any doubt that the particles causing the lighter band were protons, that is to say singly charged hydrogen atoms, with half normal energy. The presence of this type of secondary ray had already been suggested by the beading

¹ V. p. 133.

² V. p. 27.

on the hydrogen parabolas¹ and the explanation then suggested is doubtless correct.

The two bands are associated with the presence of two quite abnormally bright molecular lines due to the hydrogen molecule and the carbon monoxide molecule respectively. If a normal singly charged

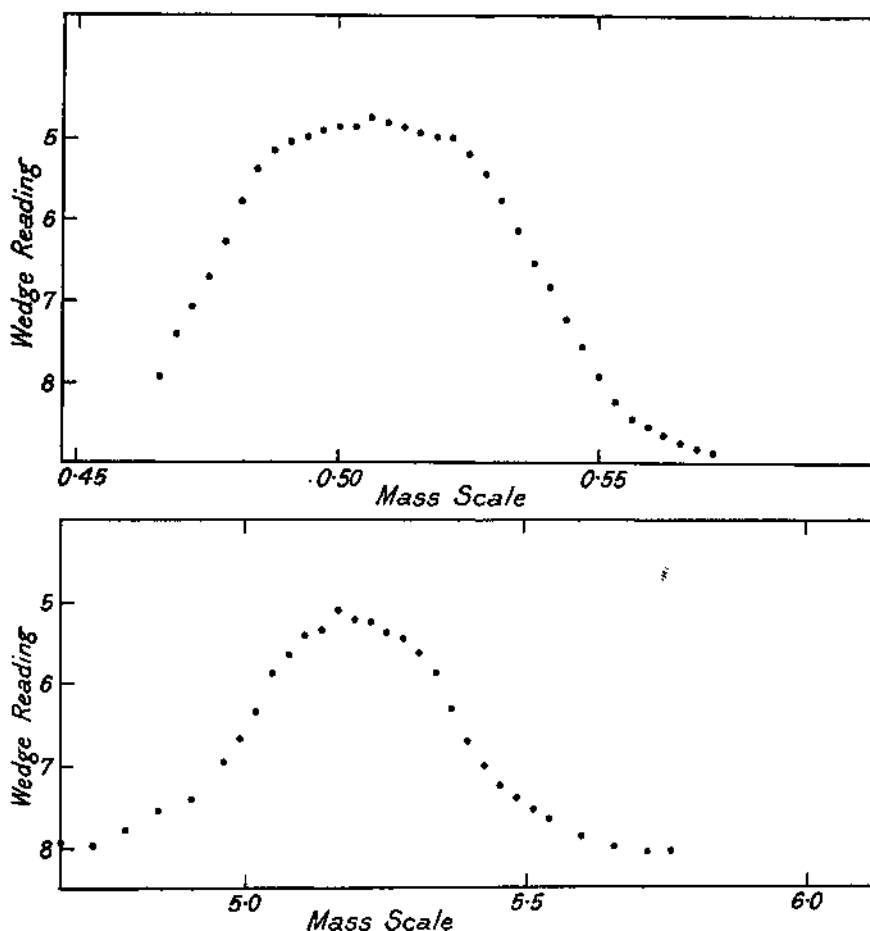


FIG. 14.—Bands in Mass-Spectra.

H_2 molecule is dissociated after it leaves the electric field and one of the atoms formed retains the positive charge through the magnetic field it will simulate a normal primary ray of mass 0.5. If we suppose that the dissociations are caused by collisions, the particles will have impressed upon them a random change in velocity and direction and so tend to form a band and not a line.

¹ Aston, *Proc. Camb. Phil. Soc.*, 19, 317, 1920.

Turning now to the case of the CO molecule here the atoms composing it have masses in the ratio 3 to 4 so that if the carbon atom retains the positive charge after the dissociation it will simulate a mass of $\frac{3}{7} \times 12$, that is 5.14. This is clearly the cause of the band observed. There is no effect at mass $\frac{4}{7} \times 16$ which leads to the very interesting conclusion that when CO^+ is dissociated the positive charge is retained by the atom of carbon in preference to that of oxygen.

Both the bands disappear completely when the pressure in the camera is sufficiently reduced, supporting the view that they are purely secondary effects and therefore not to be seriously considered in connection with the interpretation of mass-spectra. The fact that the centre of each band corresponds to a mass about 3 per cent, heavier than that deduced by the theory given has doubtless some significance. An account of these bands and their explanation was given at the Bristol Meeting of the British Association in 1930 and attention is now drawn to the phenomena again in hopes that research workers interested in the dynamics of molecular combination and dissociation may find in them a possible new line of attack.

CHAPTER VII

ANODE RAYS

61. Mass Rays of Metallic Elements.—The use of the ordinary gas discharge described in the previous chapter is clearly limited to those elements which may be introduced as vapours or vaporizable compounds into the discharge itself. A large number, including the majority of the metallic elements, are unsuitable for this treatment so that other devices must be employed to obtain their mass rays. In one or two cases the rays have been produced by direct ionization of the metallic vapour ¹ but a more generally effective method is to employ a special discharge from an anode which itself produces the rays required.

Such an anode was originally discovered by Gehrcke and Reichenheim ² who observed rays streaming from heated salts of alkali metals when these were used as anodes in discharges. This discovery was made before good means of analysis were known, but from the visual spectrum of the rays they deduced rightly that these were positively charged ions of the metals concerned. They obtained the rays, which they called " anode rays " by two distinct methods. The first, which may conveniently be 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 method by which most of their pioneer work was done depended on the use of a mixed paste of graphite and salt, a " composite anode " which was automatically heated by the discharge itself.

62. First analysis of the Alkali Metals.—This was made by the writer ³ using the hot anode method by means of the apparatus indicated in Fig. 15. The heated anode A is a strip of platinum foil welded to stout leads fused through the glass at C, the mounting being arranged so that it could be easily removed and replaced. It was heated electrically as indicated and placed immediately opposite the perforation of the cathode and about 1 centimetre away from it. The platinum strip was bent at one end into a U-shaped channel

¹ V. p. 69.

² Gehrcke and Reichenheim, *Ver. d. Phys. Gesell*, 8, 559, 1906 ; 9, 76, 200, 376, 1907 ; 10, 217, 1908.

³ Aston, *Phil. Mag.*, 42, 436, 1921.

into which salts could be fused. The discharge was maintained by a large induction coil and rectified by means of the valve V. The discharge tube was pumped out as completely as possible and then the anode cautiously heated until the discharge started. This usually happened at a 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 kilovolts. 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 direc-

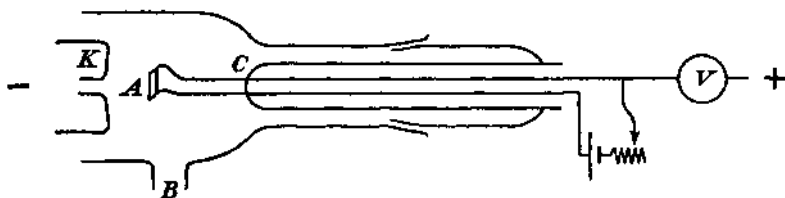


FIG. 15.—Hot Anode Discharge Tube.

tion 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.

On the other hand, as a means of identifying isotopes the method has the great merit of producing rays of the metals only. This characteristic seems to be due to the very low pressures used and also possibly to the position of the anode itself, which prevents any rays generated in the more distant parts of the tube from ever reaching the perforation in the cathode in the necessary axial direction.

The hot anode discharge was first tested by means of the parabola method of analysis and the most successful experiment was done with a mixture of sodium and lithium phosphates which 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 was announced jointly by the writer and G. P. Thomson,¹ who was then investigating rays from a composite anode. Soon after it was confirmed independently by Dempster.²

The apparatus was then attached to the first mass-spectrograph and although the beams obtained were very feeble they were sufficient to identify the mass numbers of the isotopes of sodium, potassium, rubidium and caesium.

63. Method of Accelerated Anode Rays.—The technical difficulties involved in the hot anode method gave little promise of its successful application to the metals of other groups, so after an attempt had been made to apply the vacuum arc to the problem,³ attention was again turned to the possibilities of the alternative device of the composite anode made of a paste of graphite mixed with metallic salts. This had already been successfully applied to the parabola method of analysis by G. P. Thomson.⁴ After a number of possible improvements had been tried an arrangement was found by which the mass rays could be accelerated after production. This was capable of giving beams high enough in intensity and under sufficient control to be applied to the mass-spectrograph.

The general form of the apparatus with which the best results were obtained is shown diagrammatically in the accompanying rough scale drawing (Fig. 16). The discharge tube is comparatively small and shaped as illustrated. The construction of the anode is indicated in detail on a larger scale. The graphite paste is pressed into a hole drilled in the end of a small steel cylinder. This is carried on a long brass wire so that it can be slid into a pyrex glass tube about 20 cm. long fitting it closely. The working position of the steel container is with its face containing the paste flush with the end of the tube which is cut off exactly at right angles. The thickness of the wall of the container is exaggerated in the sketch. It is actually made as small as possible consistent with strength, so that the anode looked at end on from the cathode appears simply as a graphite disc surrounded by a glass ring. Since the working of the apparatus is capricious and liable to be altered entirely in character by the slightest

¹ Aston and Thomson, *Nature*, 106, 828, 1921.

² Dempster, *Phys. Rev.*, 18, 417, 1921.

³ Aston, *Phil. Mag.*, 47, 385, 1924.

⁴ V. p. 113.

variation in the position of its parts, the anode container was so arranged that it could be withdrawn, refilled and replaced with great exactness. The best working position of the anode was as indicated. The discharge producing the anode rays took place between the graphite paste and the subsidiary cathode. The latter was an aluminium cylinder pierced for the passage of the rays and hollowed at its working surface to concentrate the cathode rays on the anode. It was mounted in a block of ebonite just in front of the earthed cathode of the mass-spectrograph.¹

During the preliminary experiments when the cathode of the discharge tube itself was earthed, it was found in the first place that good beams of anode rays could only be obtained when the pressure in the discharge tube was comparatively high and the potential conse-

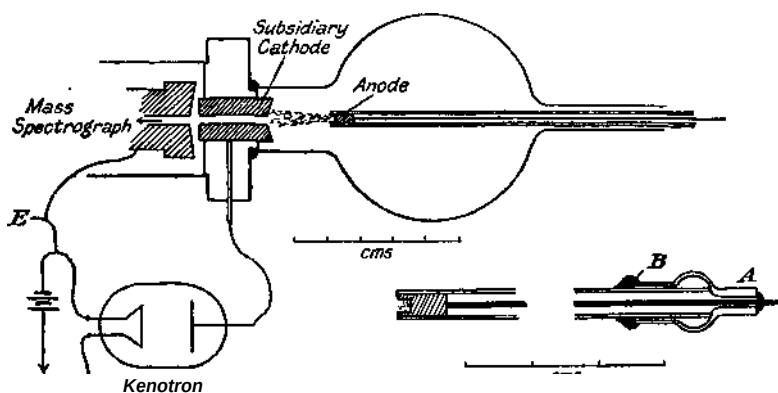


FIG. 16.—Apparatus for Accelerated Anode Rays.

quently too low to be convenient for use with the mass-spectrograph. In the second place the discharge itself was exceedingly unstable, for increase of current meant a hotter anode ; this led to the liberation of more gas which caused further increase of current. On the other hand, if the anode was allowed to get too cold, the tube went hard and ceased to conduct altogether.

Both these difficulties were overcome by the introduction of a secondary cathode connected to earth through a kenotron as indicated. For if the earthed filament of the kenotron is maintained at a definite temperature, sufficient for example to give a saturation current of 1 milliampere, it is impossible to force more than 1 milliampere through it. Hence, whatever the conditions of the discharge tube, short of absolute non-conductivity, the current through it will remain constant. It will be realized at once that this arrangement supplies

¹ V. Fig. 10.

exactly the stabilizing influence required. If the discharge tube gets harder, the potential drop between the anode and the subsidiary cathode will increase. The energy of the beam of cathode rays will increase, this will raise the temperature of the anode and soften the tube. On the other hand, if the tube gets too soft the energy of the cathode ray beam will decrease, cooling the anode and hardening up the tube again.

In addition, the main discharge can now be regulated to give rays of any required energy independent of the hardness or softness of the discharge tube. If we put a mean of 24 watts through the secondary circuit at a current of 1 milliampere, the anode will be maintained at a mean potential of 24 kilovolts above earth and the rays after leaving the subsidiary cathode will be *accelerated* to a velocity corresponding to that potential. Thus, if the potential between the anode and the subsidiary cathode is, say, 8 kilovolts, the accelerating potential will be 16 kilovolts; if the discharge potential falls to 6 kilovolts, the accelerating potential will automatically rise to 18 kilovolts and so on.

For details of the experimental procedure the reader is referred to the original paper.¹

It has not yet been found possible to obtain a beam of anode rays sufficiently strong for any mass line to be visible on the willemite screen as are the lines of hydrogen with the discharge-tube method. On this account the first three or four minutes of the discharge are generally utilized in recording the lithium lines as a necessary check on the working of the whole apparatus.

With all elements other than the alkali metals the effects are feeble, so the exposures are prolonged as far as possible until the anode dries up or it is judged that further continuation is useless. Most of the results, when the apparatus was working particularly well, were obtained with exposures of about half an hour, but in some cases the discharge was maintained for one hour and a half.

At the beginning of the discharge the anode surface is comparatively cool and glows brilliantly red showing the lithium spectrum. The bright divergent beam of lithium anode rays never lasts many minutes of the exposure. Its appearance is a good sign, but equally bright lithium mass lines have been obtained when it could not be seen at all. A valuable indication that the anode surface is functioning properly is the appearance of a small cloud of sodium light surrounding it exactly as in the case of the hot anode experiments.²

As the gases come off less and less rapidly from the anode intermittent pumping only is required to keep the pressure down and the

¹ Aston, *Phil. Mag.*, 47, 385, 1923.

² V. p. 64.

longer portion of the exposures is generally carried out without pumping at all. The anode by now has lost its lithium glow and becomes red and sometimes white hot. Lithium mass rays are probably absent at these later stages, but the lines of the heavier members of the alkali group, if they are present in the anode paste, still continue to come off with undiminished intensity and in the case of other elements the high temperature of the anode surface seems favourable and may be essential. The general glow of the discharge is dirty yellow at the start and becomes blue-grey in the later stages.

64. Experimental results.—The principal difficulty in the way of successful working of the method is complete ignorance of the mechanism of the discharge which is probably very complex. It behaves at times in the most capricious and unaccountable manner. Each time the discharge tube is altered or even taken down for cleaning entirely different results may be obtained. When by good fortune all is well the arrangement is capable of good performances. Thus, after a favourable setting of the apparatus six elements were successfully analysed in as many working days. On the other hand, after dismantling became imperative and it had been cleaned and rebuilt, exactly as before as far as one could tell, no results of any value were obtained during weeks of work.

The method appears to be capable of wide application to metallic elements. Those of Group I are much the easiest to deal with, and those of Group IV apparently the hardest. The difficulty of obtaining the mass rays appears to increase with increasing atomic weight, an effect which may be partly ascribed to decreasing velocity of the rays. The quantity of material necessary is only a few milligrams, of which much can be recovered after the experiment, so that it is particularly suitable in cases where only small quantities are available. High purity, as in other mass-spectrum measurements, is in general of quite subordinate importance.

In the matter of interpretation the results of accelerated anode rays are very nearly ideal. The ordinary discharge method gives altogether too many lines due to atoms and molecules other than those under consideration; the hot anode method gives too few, rendering measurement difficult. The method gives practically no molecular lines at all and the atomic ones generally present are just about what is required for a satisfactory system of reference, and no more. The most important of these lines are C^{12} , Al^{27} , Si^{28} , Fe^{56} , I^{127} .

Thanks to the very wide range of application of this method the mass-spectra of over twenty elements, including several of the rare earths, were successfully obtained by its use with the first mass-

spectrograph. The extension of these results to apparatus of higher resolving power will be described later.

65. Dempster's analysis of anode rays.—Dempster's original apparatus for the analysis of anode rays derived from heated salts has already been described (p. 28). His later¹ modification of the apparatus in which the metals themselves were vaporized is shown in Fig. 17. The anode is a small iron cylinder filled with metal and heated electrically by a surrounding coil of iron alloy wire. The vapour so produced is ionized by bombardment with electrons which have fallen through 30-160 volts from a coated platinum strip near the mouth of the cylinder F. The positively charged ions pass into the accelerating field through a hole in the iron plate P. The energy of the rays before acceleration is regarded as being negligibly small, so that all of them reach the slit S_1 with the same energy which can be controlled by varying the potential between P and S_1 . This potential is usually 800 to 1000 volts derived from a set of small storage cells. The rays passing downwards in a narrow beam through S_1 are bent into a semicircle by the magnetic field and so focussed upon the second slit S_2 . Here they are detected and measured by the charge they bring up to a plate as before.

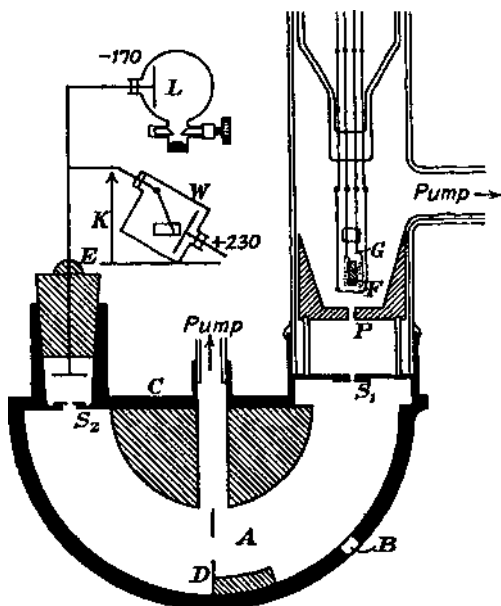


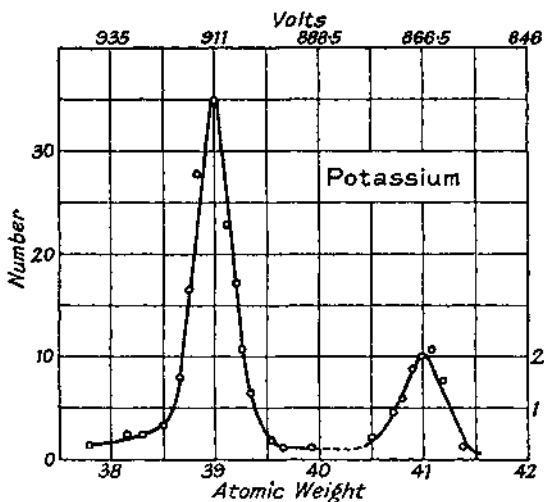
FIG. 17.—Dempster's Modified Apparatus.

Methods of measurement.—The quadrant electrometer used in the first experiments to detect the rays is replaced by a Wilson tilting electroscope and the compensating arrangement illustrated. The positive current carried by the rays to the plate is balanced by an equal negative ionization current driven to the electrode of the ionization chamber L. The electroscope is used to indicate when balance has been obtained. The novel feature of the arrangement is the method used for adjusting the ionization current to balance

¹ Dempster, *Phys. Rev.*, 20, 631, 1922.

the positive ray current. The ionizing agent is a group of old radium emanation tubes which are placed as indicated and cut off from the ionization chamber by an adjustable graduated slit. A slit width of 1 millimetre gives an ionization current of approximately 6×10^{-12} amperes. Settings for balance can be made in about 5 seconds to within $1/40$ mm.

In order to bring rays of different mass to the slit S_2 either the electrical potential or the magnetic field may be altered.¹ In practice the latter cannot be conveniently measured, so it is kept constant and the accelerating potential put through a series of measured values.



If the current reaching the plate is plotted against potential, a curve is obtained showing peaks corresponding to the different isotopes.

This change in the accelerating potential between P and S, is responsible for a serious source of error in the measurements of the relative intensity of isotopes which was not detected by Dempster in his earlier experiments. It was due to the stray electric field spreading through the hole in P and affecting the flow of the ions through it, and was later rectified by the use of gauzes.²

66. Experimental results.—A typical curve obtained in this way with potassium is shown in Fig. 18. In this experiment the peak corresponding to the stronger isotope 39 occurred at 911 volts. The whole-number rule is assumed and the maximum is placed exactly at 39, and the other atomic weight abscissae are obtained by dividing

¹ V. equation on p. 28.

² Dempster, *Phya. Bev.*, 20, 636, 1922.

39 x 911 by the potential in volts for each measurement. The current scale for the fainter isotope in the figure is made five times that for the stronger. The intensity ratio is approximately 18 to 1, giving a mean atomic weight of 39.1 in good agreement with the chemical value. The position of the peaks confirms the result obtained with the hot anode.¹ Dempster independently demonstrated the isotopes of lithium but was unable to obtain consistent values for their relative proportions in the element for the reasons already mentioned. The most important analyses obtained by this method are those of magnesium, calcium and zinc.

67. Other Sources of Anode Rays.—Other sources of positive ions suitable for analysis have been developed in recent years. Kunsman² discovered that the crystal granules used as catalysts in the synthesis of ammonia when heated emitted positive ions at a remarkably constant rate. These granules consist of a fused mixture of iron oxide with about 1 per cent, of an alkali or alkaline earth metal with sometimes the addition of about 1 per cent, of aluminium oxide. A rough analysis of the rays produced by means of a low-resolution magnetic spectrograph of the Dempster type showed that the ions were singly charged atoms of the metals concerned.³ Kunsman sources have been extensively used for experiments on positive ions, for unlike the other anode sources so far described they will work at exceedingly low pressures. On the other hand, their life seems to be limited to 1 to 2 hours and the intensity of the beams produced has, so far, not been found high enough for analyses of high resolution. It has been noticed that the strongest jets of rays from a Kunsman source, like those from the "hot anode" usually originate from the metal heater at the edge of the fused mixture rather than from the mixture itself.

This fact led Moon and Oliphant⁴ to prefer as a source a heated tungsten filament immersed in the vapour of the metal. The theory of this has been discussed by Langmuir and Kingdon⁵ who predict perfect efficiency—that is, all the atoms striking the filament will be ionized—when the work function greatly exceeds the ionization potential. Both in steadiness and intensity this form of source is admirable, but unfortunately its scope is limited so far to a few easily ionizable metals which can be conveniently vaporized.

¹ V. p. 65.

² Kunsman, *Science*, 62, 269, 1925; *Proc. Nat. Acad. Sci.*, 12, 659, 1926.

³ Barton, Harnwell and Kunsman, *Phys. Rev.*, 27, 739, 1926.

⁴ Moon and Oliphant, *Proc. Roy. Soc.*, **137A**, 463, 1932.

⁵ Langmuir and Kingdon, *Proc. Roy. Soc.*, **107A**, 61, 1925.

CHAPTER VIII

METHODS OF PRECISION

As theory discussed later will show, the Whole Number Rule established by the first mass-spectrograph was never supposed to be mathematically exact. Although the deviation was only measurable with any accuracy in the single case of hydrogen it was soon clear that the masses of the lithium isotopes 6 and 7 exceeded whole numbers by at least 1 part in 1000, the mass of carbon being taken as exactly 12, while those of other atoms such as Fe 56 appeared to be less than whole numbers.¹

68. Costa's Mass-spectrograph.—The first attempt to measure these deviations by measurements of an accuracy greater than 1 in 1000 was made by Costa who in 1925 published results obtained by means of a mass-spectrograph set up in Paris.² This instrument was identical in principle with the first mass-spectrograph, but included certain refinements which enabled its designer to claim for it comparisons of mass to an accuracy of 1 in 3000, that is to say, three times greater than that previously attained. With this apparatus Costa compared, by the method of bracketing³ Helium with Hydrogen, Helium with Carbon, Helium with Lithium 6 and Nitrogen with Lithium 7. His work on lithium is of the greatest importance. In it he overcame the very serious experimental difficulties of recording the mass rays of lithium and those of nitrogen in the same discharge tube by means of a movable anode. The values of the two lithium isotopes recalculated from his ratios are the only accurate ones we have. Their reliability is supported by the fact that the other ratios he measured for H, He and C have been since confirmed to be within the accuracy he claimed.

69. The Second Mass-spectrograph.—Improvements in the design of the first mass-spectrograph had been under consideration as early as 1921. It was realized that the accurate determination of the divergences from the whole-number rule, now called packing fractions, was of fundamental importance since this is one of the few avenues by which the problem of the structure of the nuclei of atoms could be approached. Every effort was made to push the precision

¹ Aston, *Phil. Mag.*, 45, 941, 1923.

² Costa, *Ann. Physique*, 4, 425, 1925.

³ V. p. 50.

of analysis to its practical limit. It was finally decided that the increase of resolving power could best be obtained by doubling the angles of electric and magnetic deflexion and using finer slits placed farther apart. Special methods were devised for increasing the accuracy of comparison. These objects were successfully carried out. The improved instrument set up by the writer in the Cavendish Laboratory in 1925, and still in use, has five times the resolving power of the first one, far more than sufficient to separate the mass lines of any element known. Its accuracy is 1 in 10,000, which is just sufficient to give rough first-order values of the divergences from whole numbers. The general appearance of the instrument can be gathered from the photograph and the details of its construction from the diagram (Fig. 19) which is drawn approximately to scale.

70. The Slit System.—The two slits S_1 , S_2 , which collimate the rays are of the same construction as before.¹ They are made as fine as possible consistent with reasonable exposures; the pair in use at present are about 0.02 mm. wide. Their distance apart is 20 cm., double that in the old instrument. They are mounted at the ends of a brass tube which also carries the cathode. This tube is supported at one end by its tip which fits accurately into

¹ V. p. 43.

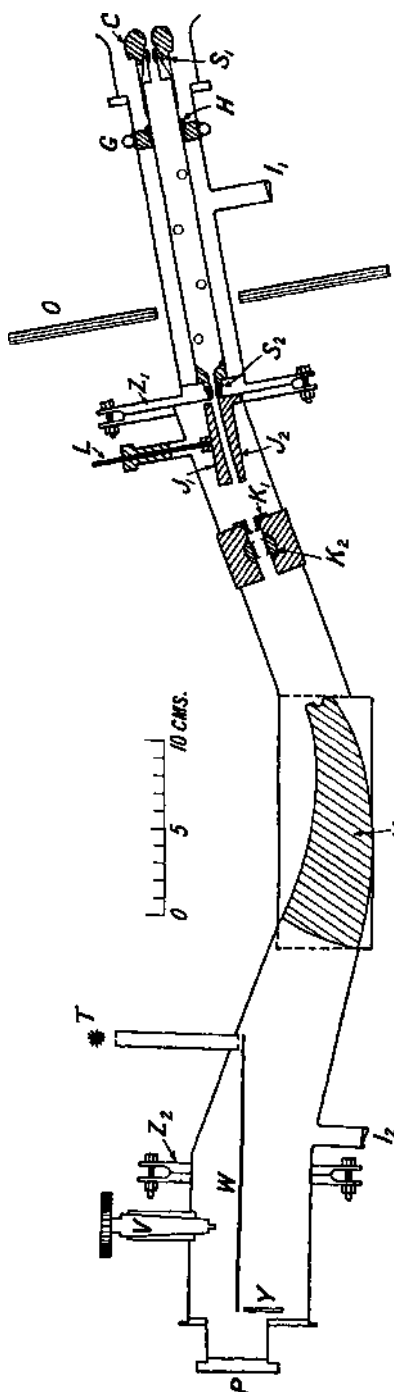


FIG. 19.—Diagram of Second Mass-Spectrograph.

a hole in the brass plate carrying the electric deflexion system, and at the other by a ground joint H as indicated. By merely removing the discharge tube it is thus possible to examine or change both slits. A bayonet fitting ensures the carrier tube coming into exactly the same position every time it is replaced.

71. The Electric Field.—For the purpose in view it was desirable that this should be as efficient as possible since the higher the potentials necessary to deflect the rays through the large angle, one-sixth of a radian, the more difficult they would be to produce, to apply and to measure. The plates were, therefore, curved and placed very close together. They were machined out of brass. The acting surfaces were ground accurately to 30 cm. radius, 1 cm. wide by 5 cm. long, and held 1.25 mm. apart by glass distance-pieces bearing on flats machined outside the curved faces. The lower earthed plate J_2 was bolted to the outer disc of the special joint Z_1 in such a way as to be capable of small adjustments both up and down and in rotation. The upper plate J_1 was clamped rigidly to the lower one by insulated screws and could be raised to the required potential through the insulated lead L. By the removal of this and the breaking of the special joint Z_1 and the connections for supply and exhaust of the discharge bulb, the whole of the electric system could be removed for examination or adjustment. It can be easily calculated from these dimensions that the ratio of the energy of the ray in volts to the potential applied to the plates causing deflexion through one-sixth of a radian is 120 to 1. This means that 400 volts is sufficient to deal with 48 kilovolt rays, about the hardest ever used. The potentials were derived from a set of 500 small accumulators built specially for the purpose.

72. Special Joints.—It is clear that for the purpose in view rigidity of a high order is imperative, and for this reason the body of the apparatus was made of wide thick-walled brass tube permanently soldered together wherever possible. Demountable joints must be provided, however, and in order to secure vacuum tightness and rigidity these require careful design and construction. Costa used ground joints. The type of joint, Z_1 , Z_2 , shown is very convenient. It is easier to construct than a ground joint, and is of wider scope. It consists of two brass discs of liberal diameter turned with a small projection on their faces which keeps them concentric when locked together. The disc must be so thick that a deep groove, the wider the better, can be cut away without endangering the mechanical strength of the rims which are bolted together as shown. The mechanical strains are taken by the bolts while vacuum tightness is ensured by running a thin coat of soft Everett wax into the groove.

When the joint is to be opened the seal is cracked cold, and when put together again it is usually only necessary to run a pea flame round the groove to ensure tightness. The most important point is **for** the bolts to be so far from the wax that they do not interfere with its accessibility to the flame or to the view of the operator.

The quantity of the electric spectrum of the rays allowed to pass into the camera was controlled by fixed and movable diaphragms K_1 , K_2 exactly as before. K_2 is mounted in a long and accurately ground taper plug of brass. The lever turning the plug is provided with a scale so that the aperture of the diaphragm can be set with great accuracy.

73. The Magnetic Field.—As before, the instrument was built round its most massive member, the magnet, which was specially designed for the purpose. The core was a ring of special magnet steel of rectangular cross section 15 cm. by 5 cm., with an external diameter of 46 cm. It was cut into three sections, a lower half and two upper quadrants. Between the upper ends of the latter a sector 5.2 cm. wide was removed to make place for the pole pieces of the mass-spectrograph. The three sections of the core were equipped with large brass end plates by which they could be bolted together. Since the principal object was to ensure an extremely constant field for considerable periods, a minimum heating effect was desired both on account of this affecting the resistance of the windings and also the permeability of the core. This was obtained by winding the whole ring as lavishly as possible and so reducing to a minimum the watts per gramme of copper necessary to produce a given field. By continuing the winding right up to the pole pieces a second valuable result is obtained, namely, the decrease of the stray field; the discharge is further protected from this by soft iron plates at O.

The pole pieces form part of the walls of the mass-spectrograph itself into which they were soldered vacuum-tight. Their rectangular outside section, indicated in the figure, registered with that of the core ring, and they were machined away smoothly so that the actual pole faces were of the greatly reduced sickle-shaped section shown at M. By suitable massive distance-pieces these faces were held 3 mm. apart. At the point of entry of the bundle of rays small semi-circles were machined from the pole pieces in an attempt to achieve second-order focussing,¹ but it is not yet certain whether any real advantage has been gained by this.

The length of the path of the rays in this highly concentrated field is about 15 cm. The radius of curvature of the median ray is about 22.5 cm., so that the deflexion of a singly charged mercury atom with 30 kilo volts energy will require 15,700 gauss. This can be

¹ F. W. Aston and R. H. Fowler, *Phil. Mag.*, 43, 523, 1922.

attained by the use of less than twenty watts and the effect of any small creep in its value is eliminated by the particular methods of measurement employed. Below 10,000 gauss the field is practically proportional to the current, making it a simple matter to calculate the value of the latter necessary to bring a known mass to any required point of the spectrum.

74. The Camera.—The camera is made in two halves connected by a joint of the special kind described. The mechanism, not shown in the figure, for supporting the plate W, is mounted on the movable half so that it is only necessary to break one joint to enable any vertical adjustment to be made during the operations of focussing. Horizontal movement of the plate parallel to itself is achieved as before through a vacuum-tight plug, V. The plate itself is a slip 2 cm. broad and 16 cm. long cut from a half-plate, and will easily accommodate six spectra.

A technical detail which has added greatly to the convenience of the operation of plate-changing is the direct attachment of the plate-glass window P to the tubular extension of the camera with Everett wax instead of a greased ground joint as before. The circular plate of thick glass is ground at the edge so that it projects slightly into the tube which it fits. The shoulder butted against the tube takes the strain of atmospheric pressure, and the small quantity of wax necessary runs naturally into the outer right-angle corner giving a perfect lute. When it is required to change the plate, after air has been admitted to the camera, the wax joint is broken cold by a tap with a wooden pocket rule. The plate is changed and the window replaced at once as exactly as possible. The wax is resealed by running a small gas flame round the joint. The flame itself supplies the light necessary for the operation which only requires a few seconds and can be repeated scores of times with the same wax. The arrangement of the willemite screen Y and the lamp T for recording a fiducial spot on the plate are exactly as before.

75. Vacuum Technique.—The first method used for obtaining the very low pressure required in the slit system and camera was charcoal cooled in liquid air, as in the first mass-spectrograph. Recently it was decided to try the effect of substituting a modern high-speed mercury diffusion pump. For testing this a Dushman ionization gauge was attached to the camera. This showed that under normal working conditions with cooled charcoal the pressure in the camera was about 01 microbar—about that expected and previously estimated—while the discharge was in action. If the discharge was stopped and the bulb evacuated, the pressure sank in a few hours as low as 0.025 microbar.

On attaching the diffusion pump to the camera the improvement was not very great, 0.04 microbar with the discharge running, but when instead it was attached to the slit system its superiority over the cooled charcoal was very pronounced. The camera pressure dropped rapidly to 0.02 microbar and on one occasion to 0.008 microbar. These tests show that the pressure in the camera is determined not so much by the vapour pressure from its surface as by the diffusion leak through the slit system, and that, when a diffusion pump is fitted to the latter, cooled charcoal is sufficient for the camera itself.

76. Polarization of the Electric Plates.—When the apparatus was first set up for preliminary tests an anomaly was noticed which caused some misgiving. This was that the curvature of the lines, observed in the original instrument but never satisfactorily explained, now appeared enormously exaggerated. This effect was soon found to be associated with an entirely unexpected and very serious difficulty. The instrument had been primarily designed to compare masses by the method of coincidence¹ which depends on the theorem that if the magnetic field is kept constant and two mass lines are taken with different electric fields, masses whose ratio is the inverse ratio of the electric fields will give lines coinciding exactly. This theorem had been tested by means of the lines of the atom and molecule of hydrogen using the bracketing method on the original mass-spectrograph, and found to give results correct to the accuracy then attained. When the atomic and molecular lines of hydrogen were tested in this way on the new apparatus a discordance was observed not merely measurable but absurdly large, several parts in 1000.

After months of disappointing work it was found that the cause was a polarization of the surfaces of the plates which might take as long as 0.05 second to rise to its maximum value. Drastic scrubbing with emery paper reduced the effect temporarily and also the curvature of the lines which is due to the same cause, and the plates were later heavily gilded. With a clean gilded surface the effect was reduced to manageable proportions. Arrangements were now made to measure it with the highest accuracy possible. This was done by means of the hydrogen lines in the following manner. A special rotating contact breaker was made by which a voltage V , then a second voltage $V + h$ slightly different, and, finally, the two in series $2V + h$ could be applied rapidly over and over again. The length of the exposures at the first two potentials, giving lines of the molecule, relative to the third, giving the line of the atom, could be controlled and were adjusted to give lines of equal intensity. A ratio of precisely 2 to 1 should give three lines forming an exactly

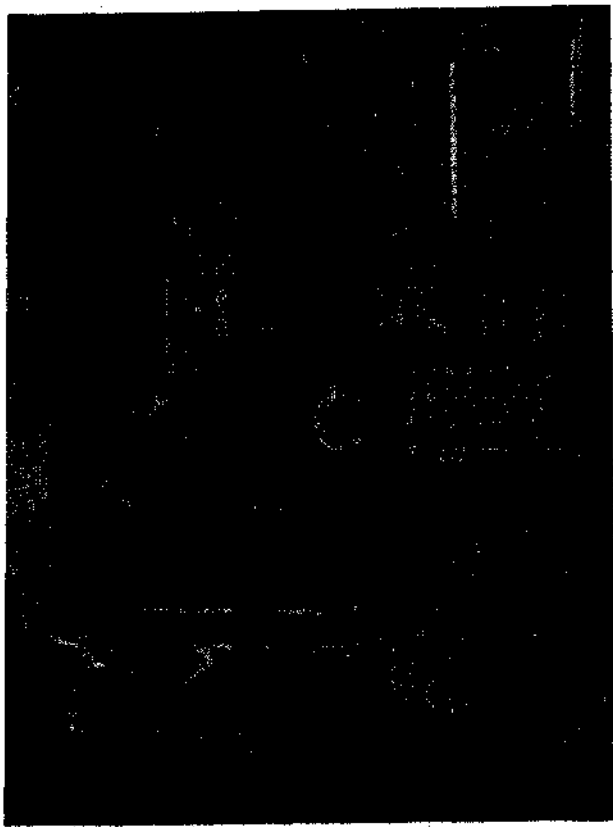
¹ V. p. 48.

symmetrical bracket. This device eliminates the necessity of keeping the magnetic field absolutely constant since the electric fields are changed so rapidly that small changes will only lessen the sharpness of the lines and not alter their relative positions. It also makes it unnecessary to measure any potential at all so long as h is less than 1 per cent, of V . It is, in fact, the exact counterpart of finding the mid-point of a line with a pair of dividers, and like this can, unfortunately, be applied only to ratios of 2 to 1. Measured by this means and allowing for the electron correction, the polarization effect, even with clean gold surfaces, was found to be still as high as 5×10^{-4} , much too high to be neglected. Experiments made while it was very much greater had, however, shown that it remained very constant so long as the conditions of discharge were not altered, so it was decided to eliminate it as far as possible by using the rays themselves to measure the ratios of the field strengths.

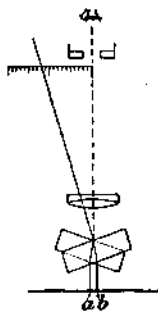
77. Performance of the Instrument.—The general appearance of the mass-spectra obtained by means of the instrument in its present adjustment is shown by the reproductions on Plate V. The spectrum photographed is nearly 16 cm. long and includes slightly more than one octave of mass. As Spectrum VI clearly shows, the distribution is surprisingly linear all along. The dispersion scale varies from about 1.5 mm. at the most deflected end, to rather more than 3 mm. at the least deflected end, for a change of mass of 1 per cent. Hence, in the middle portion of the plate the scale is about as open as that of a twenty-inch slide rule. The resolving power is sufficient to separate lines differing by 1 in 600 and as expected from the theory is not very different at the two ends. Since the lines are irregularly curved and change their shape as one moves from one end of the spectrum to the other, it is impossible to assign positions to them relative to the fiducial spot with sufficient accuracy to approach the figure of 1 in 10^4 aimed at. This can only be done by measuring the distance between lines of approximately the same intensity, and therefore the same shape, when they are quite close together.

78. The Comparator.—Of several methods tried, the most convenient for making such a measurement is by an application of the principle of Poynting's Tilting Plate Micrometer.¹ If an object is observed through a thick plate of glass and the plate tilted, the object will appear to shift. Poynting showed that for moderately small angles, this shift is very exactly proportional to the tangent of the angle of tilt. For the present purpose, two plates are used with their edges touching. Their plane of separation is arranged to be along the middle of the spectrum, which is observed directly below. The

¹ J. H. Poynting, *Phil. Trans., A*, 204, 413, 1905.



THE SECOND MASS-SPECTROGRAPH.



plates are so connected by a simple mechanism that they move through equal and opposite angles, giving double the range of a single plate, and affording complete optical compensation for focus, so that fairly high powers of magnification can be used when calibrating with a standard scale. To measure the distance between two neighbouring lines a and b (Plate V), these are observed through a suitable low-power lens and the plates tilted until the edge of the right half of a coincides with the edge of the left half of b , giving the appearance of a single line if the intensities are equal. The tangent reading is taken and the operation reversed until the edge of the left half of a coincides with the edge of the right half of b . The sum of these two readings from the central zero is a measure of the distance and can be calibrated once and for all by the use of a standard scale. The great advantage of this over other types of comparator, for this particular purpose, is that the setting is practically independent of small changes in the position of the eye of the observer. By a lateral movement of the eye one can shift the dividing plane right across the narrow spectrum, and so compare any part of one line with the corresponding part of the other. This enables much more reliable readings to be obtained with irregularly shaped but similar lines than would a fixed line of division. A photograph of the instrument itself is shown in Plate V. It is at present fitted with two echelon plates 1 cm. thick. The measuring arm is 30 cm. long, and the tangent scale divided into millimetres 78.5 of these correspond to 1 mm. shift. With sharp lines the accuracy of setting is well within 0.01 mm., but the range is small, a little more than 2 mm. The fainter the lines on these spectra the sharper they are, so that the best measurements are to be obtained from lines just strong enough to be clearly seen. In order to increase contrast, the plates are laid face down on glazed process paper and observed by reflected light. In some cases the negatives were intensified before measurement. The position on the spectrum of the pair of lines to be measured is at our disposal, and is chosen to suit the particular system of measurement employed. All the most accurate determinations were made in that part of the spectrum where the dispersion constant is about 3 mm. for 1 per cent, change of mass.

79. Methods of measuring Ratios of Mass.—The accurate comparison of two masses giving lines on a mass-spectrum depends on the determination of two quantities, the distance between the lines, and the dispersion constant. The first must be small, and is measured directly by the comparator as described. The second is arrived at indirectly by approximate measurements of large intervals between lines whose mass differences are known with sufficient certainty.

The hydrides of carbon and oxygen are most useful for this. From these data, the dispersion constant for several points on the small range actually used can be plotted. These lie on a straight line, so that interpolation is easy. Values of the dispersion constant appear reliable to about 0.3 per cent. They are only constant for one setting of the apparatus, and must be confirmed or recalculated if any change is made. It will be seen that if the interval between the lines corresponds to a difference of mass of less than 1 per cent., and no other errors are present, an accuracy of 1 in 30,000 can be looked for. These measurements can be applied in a number of different ways to suit particular cases, the principal ones so far used can be classified as follows :

Method I.—Direct measurement on a single spectrum. This method is virtually free from all uncertainty and independent of the polarization error, but can only be applied to bodies giving lines clearly resolved, but differing by less than 1 per cent, in mass. These cases are unfortunately very rare. The best example is the doublet given by oxygen, methane shown in Spectra I and IV. Here the lines only differ by 0.2 per cent, in mass, and can be obtained of equal intensity by manipulation of the quantities of oxygen and methane present in the discharge tube. Other cases will be noted later as they occur.

Method II, which may be called the method of series shift, can be employed whenever the masses to be compared form terms in a series whose unit of difference is not too great. Two potentials are chosen which will bring consecutive terms into the desired contiguity, and these are applied to the electric plates alternately during the exposure while the magnetic field is kept constant. The relative duration of the application of the potentials is adjusted to give, in the double spectrum produced, equal intensity to those two lines between which the interval is to be measured. A good example of this is afforded by the lines of bromine and its hydrides. These give a series 79, 80, 81, 82, shown in Spectrum V. First potentials 300 and 324 volts were applied alternately, giving four times longer exposure to the latter to compensate for the weakness of the HBr lines. In this way, Spectrum IIa was produced on which the small intervals 79, 80 and 81, 82 could be measured. The same operation was then repeated with the relative exposures reversed, giving Spectrum 116 and the interval 80, 81. Now, it is obvious that whatever the value of the dispersion constant, so long as its variation along the plate is smooth, if the four lines form a true progression, the interval 80, 81 must be the mean of the intervals 79, 80 and 81, 82, each of which correspond to the addition of one hydrogen atom. When, as

in this case, it is not, the divergence from the mean so measured gives at once the relation between the masses Br^{78} and Br^{81} required.

Method III.—This is the method most generally applicable for which the instrument was designed. It is the original bracketing method modified by the use of small intervals instead of brackets. If we wish to find the ratio of an unknown mass a ; to a known mass x we must photograph their respective lines in virtual coincidence, that is to say near enough for exact determination of the interval as described above. This is done by applying suitable potentials V_1, V_2 whose ratio differs by about a half per cent, from the expected ratio $x : a$. As we cannot trust the deflecting fields to be exactly-measurable by the potentials applied, on account of the polarizing effect, two other masses must now be found, b and c , whose ratio is identical or nearly so with $x : a$. The small interval x, a is photographed at the most advantageous position on the plate by applying the potentials V_1, V_2 in rapid succession alternately, keeping the magnetic field H_x constant. Then, using the same pair of potentials and a different magnetic field H_2 , the small interval b, c is photographed on another spectrum. The magnetic field in this case is so chosen as to bring both intervals into the same region of the plate to diminish as far as possible errors due to the values of the dispersion constant. The intervals of length are now measured and transformed into intervals of mass by multiplying by the dispersion constants calculated for the mid-point of each interval. From the value of the interval b, c , so determined, and the known ratio of the masses concerned the effective ratio of the fields can be exactly calculated and then applied, by means of the interval x, a , to determine the mass x . In practice it is not usually necessary to evaluate the ratio of the fields, for the masses concerned are all so near whole numbers that the divergence of x from a whole number is simply the difference between the mass intervals, corrected by additions or subtractions of the known divergences of the other masses used. If the agreement between the ratios $x : a$ and $b : c$ is only numerically approximate, and the approximation of suitable order, the voltage ratio is adjusted to be between them and the sum of the mass intervals used. The accuracy in this case will not be so high. An example of this method of comparison will be seen in Spectra III and IV. The first is a double spectrum taken with methane using a potential ratio between 15:12 and 24:19. The second is taken on the same plate with the same potentials after the magnetic field had been increased and BF_3 introduced. The sum of the intervals seen at the right hand of the spectra gives the relation between carbon and fluorine.

80. Experimental Results.—It will be seen that what is actually-measured by these methods is the small difference between two close ratios of mass. The most convenient method of expressing these results is the quantity called the "packing fraction" which is the divergence, plus or minus, from the whole-number rule, of the neutral atom, expressed in parts per 10,000. This requires few significant figures and has the additional advantage that its experimental error is nearly the same for atoms of widely different masses.

The instrument has been in use for seven years during which time it has yielded many valuable results. Not only have the packing fractions, and therefore the isotopic weights, of over a hundred atoms been determined, but the first isotopic analysis of mercury, lead, molybdenum, tungsten, osmium, ruthenium, thallium, uranium, niobium and tantalum have been made and in addition new isotopes have been discovered in sulphur, germanium, chromium, strontium and barium. The application of it to the problem of relative abundance will be discussed in the next chapter.

DESCRIPTION OF THE MASS-SPECTRA REPRODUCED IN PLATE VI

I.—Single spectrum of the C_1 group, showing oxygen methane doublet.

II.—Double spectra illustrating comparison of Br lines by Method II.

III.—Double spectrum comparing CH_3 and C, voltages 280, 352. The oxygen methane doublet is seen on the extreme right.

IV.—Double spectrum comparing F and C_2 , voltages 280, 352. This combined with III gives the mass of fluorine in terms of carbon and hydrogen by the general Method III. The line of B^{11} can be seen and, very faintly, that of B^{10} . The oxygen methane doublet is shown very clearly in the lower potential spectrum.

V.—Single spectrum taken with CH_3Br showing the pairs of lines due to Br, HBr, CH_2Br , CH_3Br and the second-order mercury group.

VI.—Double spectrum comparing Br^{81} with CO_2 , voltages 300, 324. The higher voltage spectrum, which had an exposure of half an hour, shows the triply-charged Br line at 26.3. It contains the lines of sulphur, chlorine, etc., and is an admirable illustration of the linear distribution of lines differing by one unit.

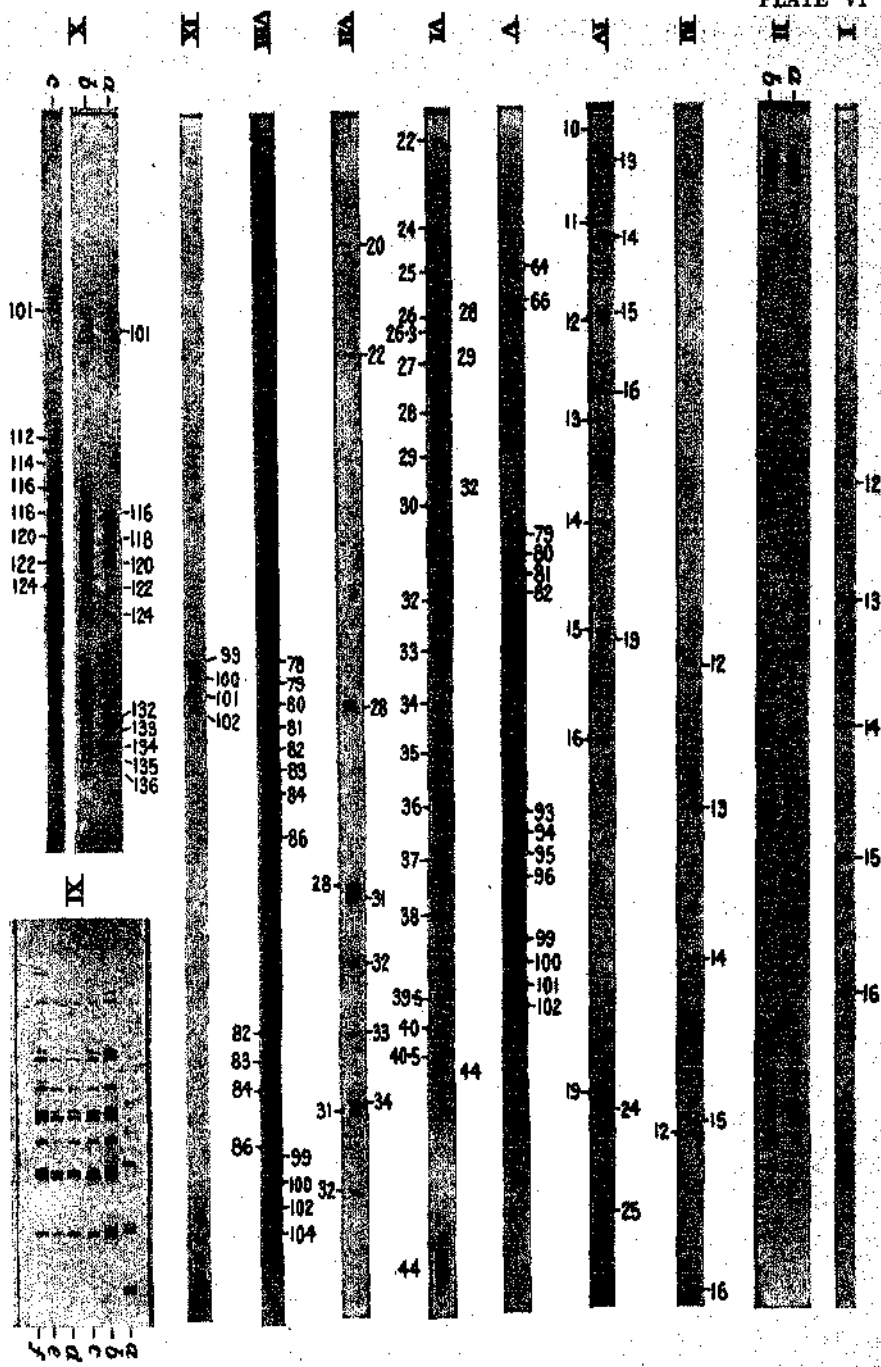
VII.—Double spectrum showing the lines of phosphorus and its hydrides photographed between the lines of carbon monoxide and phosphorus.

VIII.—Double spectrum comparing Kr^{86} with Hg^{198} . The lines of krypton are seen near the middle. The second-order lines of mercury are shown under high dispersion.

IX.—Spectrum showing the second-order mercury group very clearly.

X.—(a) and (6) Spectra showing the even spacing of the tin monomethyl and xenon lines, (c) The same with long exposure showing eleven isotopes of tin.

XI.—Six double spectra taken with the same voltages 360, 368. Each has an exposure suited to a particular pair of lines, for comparison of CO_2 , Kr and Br. (a) $Kr^{86} : CO_2$, (b) $Kr^{78} : Kr^{80}$ and $Kr^{80} : Kr^{82}$, (c) $Kr^{80} : Kr^{82}$ and $Kr^{82} : Kr^{84}$, (d) $Kr^{82} : Kr^{84}$, (e) $Kr^{84} : Kr^{86}$, (f) after addition of methyl bromide, $Br^{79} : Br^{81}$.



MASS-SPECTRA TAKEN WITH THE SECOND MASS-SPECTROGRAPH, 1925, 1926, 1927.

81. Bainbridge's Apparatus.—The apparatus with which Bainbridge has obtained such valuable results during the past few years was built in the laboratory of the Bartol Research Foundation of the Franklin Institute. A preliminary description of it appeared in 1930.¹ It was originally intended to work on the principle used by Dempster,² and to extend his work to the heavier elements. As this requires semicircular focussing together with much increased resolution its main feature is a very large electromagnet. This is so designed as to give a uniform field, up to 15,000 gauss, over a semicircular area of 40 cm. diameter with a 1.8 cm. gap. To give 12,000 gauss 870 watts are required, and to dissipate this energy ample water

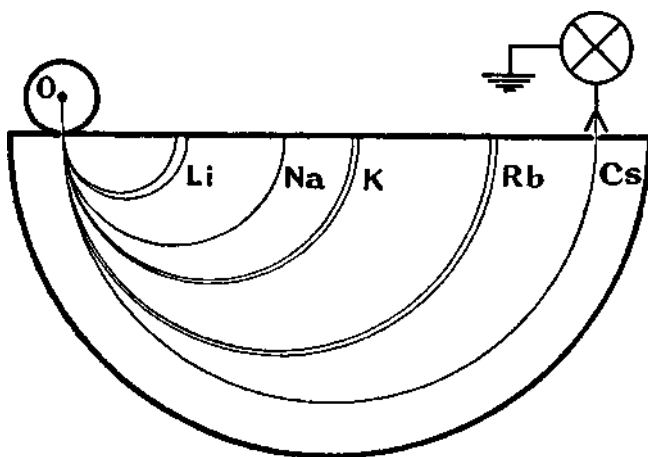


FIG. 20.—Diagram of Analysis of Alkali Metals.

cooling is provided. Up to 8000 gauss the flux density is proportional to the current.

The apparatus was first used to investigate the isotopes of the alkali metals³ and the blackening effect of their ions on photographic plates.⁴ For this work it was arranged as indicated in the diagram (Fig. 20). Heated natural silicates of the elements provided the ions and were coated on a platinum strip forming the hot anode source at 0. These ions were then accelerated by potentials up to 2000 volts to give a homogeneous beam of mass rays which were analysed by the magnetic field as indicated in the diagram exactly as in Dempster's apparatus. The current carried by the rays was collected and measured by an electrometer as shown. On account of the high resolving power available it was possible to make a critical search

¹ Swann, *J. Frank. Inst.*, 210, 751, 1930.

² V. p. 28.

³ Swann, *J. Frank. Inst.*, 212, 317, 1931.

⁴ V. p. 90.

for unknown isotopes, and measure the relative abundance of the isotopes of lithium more accurately than hitherto possible.

82. Method of the "Velocity Selector."—The number of elements to which the arrangement described above can be applied is very limited and to extend the use of the instrument to mass rays produced by ordinary discharges Bainbridge applied to it a new and original principle illustrated in Fig. 21. In this the stream of rays to be subjected to semicircular focussing is not homogeneous in energy, as in Dempster's method, but homogeneous in velocity. The

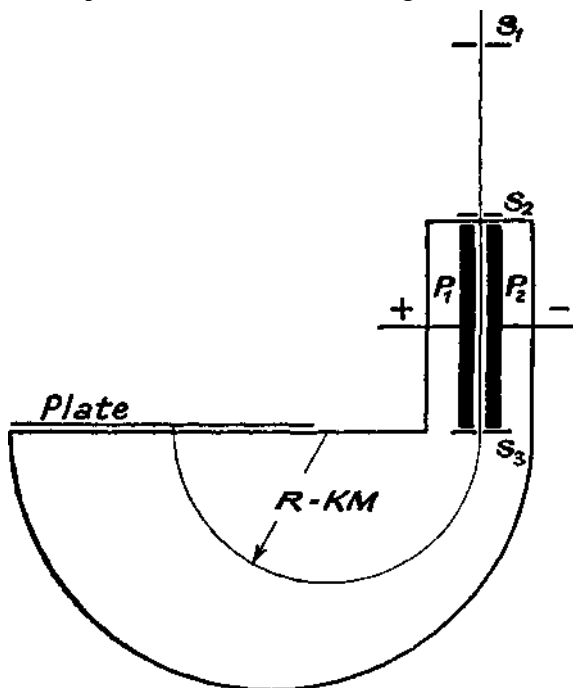


FIG. 21.—Diagram of Velocity Selector.

beam of ions produced by an ordinary discharge is collimated by the slits S_1 , S_2 and then passed through a "velocity selector" in which their deflexions are balanced by opposed electric and magnetic forces. Ions which traverse this section of the apparatus without deflexion all have the same velocity v , proportional to X/H , within narrow limits, where X is the electric force between the plates P_1 , P_2 and H is the magnetic field intensity perpendicular to the electric field. The ions which emerge from slit S_3 at the far end of the velocity selector are introduced into a uniform magnetic field, the camera section of the apparatus, and fall upon the surface of a photographic plate after describing a circular path for 180° . The radius of curvature

of a mass m with charge e is proportional to mv/eH where H is the magnetic field in this region, that is to say proportional to the mass of the ion, so that the mass scale is linear.

83. The Discharge Tube and Velocity Selector.—Fig. 22 is a drawing to scale showing details of the apparatus. Gas is admitted to the discharge tube A through P which leads to a hole under the

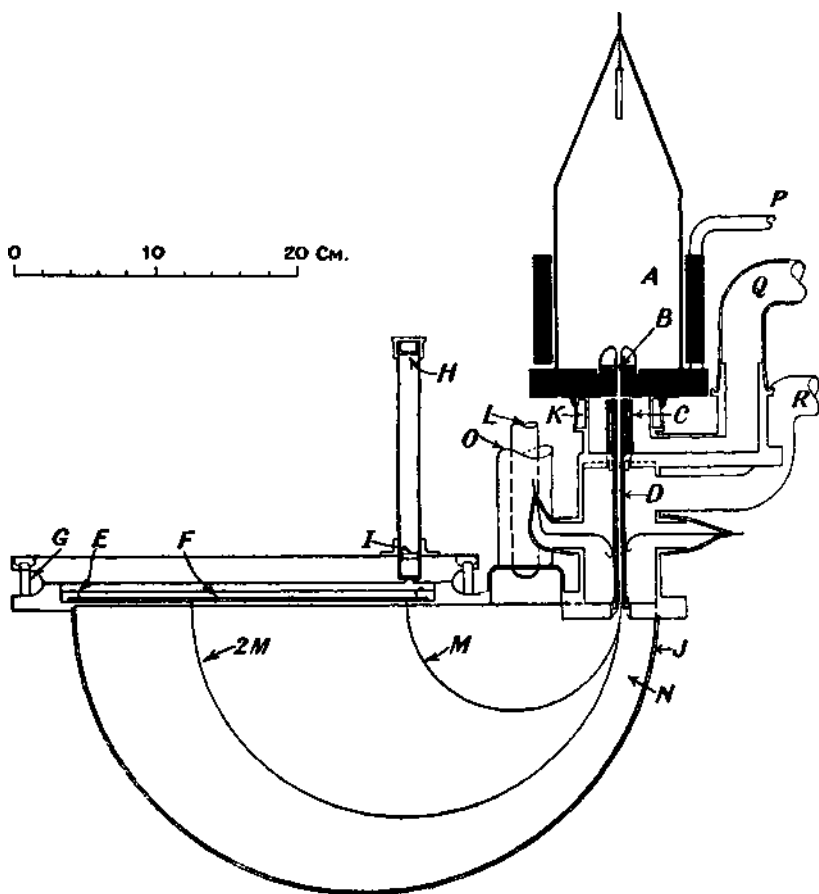


FIG. 22.—Diagram of Bainbridge's Apparatus.

cathode. The anode is a short piece of aluminium rod which is maintained at a potential of 5000 to 20,000 volts. Two 25,000-volt transformers controlled by an induction regulator provide the current for the discharge. The output of each transformer is rectified by a separate kenotron to obtain full wave rectification; it is not filtered in any way. The positive ion sheath is generally from 2 to 5 cm. above the cathode. The ions pass through the centre of the cathode on

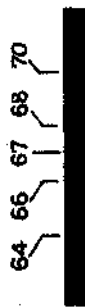
to a slit B which is adjustable and is usually set at a separation of 00025 to 00075 cm. Magnetic shielding is shown in black and consists of a cylindrical soft iron shield around the discharge tube, an iron base for the tube itself, which also acts as a cathode, and concentric iron cylinders and plates which shield the beam to within 1 or 2 mm. of the first slit of the velocity selector. The intermediate region between the discharge tube and the velocity selector is evacuated through Q by a fast condensation pump.

The ions enter the velocity selector D through a slit formed by two 10 mil bronze plates separated by 0005 cm. The plates of the velocity selector are made of brass 10 x 1 X 0.5 cm. and are 3 mm. apart. The greatest care was taken to ensure that they should be strictly plane, parallel to each other, and to the slit B. The velocity selector chamber is evacuated through R. Radio batteries supply the potential to the plates and were found satisfactorily constant. Condensers are connected across the velocity selector terminals to earth to absorb any potentials induced or picked up by the connecting leads to the battery.

84. The Camera.—The ions which emerge from the velocity selector enter the camera section where the magnetic field is uniform and the poles are denoted by N. The poles are separated 1.6 cm. by brass distance-pieces. The pole faces, including the auxiliary poles of the velocity selector, are of thick soft steel. The camera is made vacuum-tight by a thin copper jacket J. It is evacuated through O and at the same time liquid air is placed in L which acts in effect as a fast pump for condensible vapours. The photographic plate F, 25.4 x 2.54 cm. is placed in the holder E and may be moved sideways for successive exposures. Two alternative diaphragms can be placed in front of it, one allowing 10 exposures of 1.8 mm. traces, the other 5 or 6 exposures of 3 mm. traces. As a fiducial mark the slit H is photographed on the plate F by means of the lens I. After insertion of a plate the camera cover centred by four machined pins G is replaced and is luted with a coat of Glyptal lacquer, which Bainbridge prefers to wax.

85. Performance of the Instrument.—Some of the mass-spectra obtained by Bainbridge are illustrated in Plate VII and show the remarkably clean and straight lines produced. The mass scale is linear and for a mass difference of 1 per cent, the dispersion varies from 1.6 mm. at one end to 3.8 mm. at the other. These figures compared with 1.5 and 3 for the second mass-spectrograph¹ show a definite increase in dispersive power and for the accurate determination of masses Bainbridge's method has several distinct advantages. In the first place, the rays strike the photographic plate normally,

¹ V. p. 78.

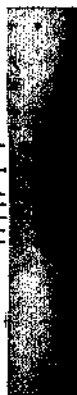


Zinc.



Germanium.

122 123 124 125 126 128 130

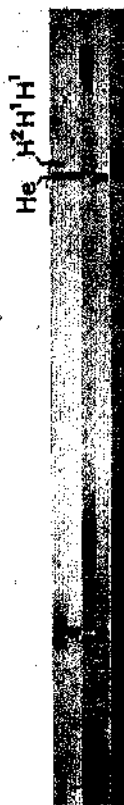


Tellurium.

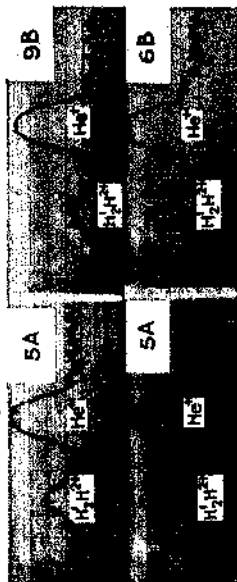


Beryllium.

Hydrogen and Helium.



Hydrogen Isotope of Mass 2.



Photometer Traces.

He^{++} , H_2



eliminating possible errors due to irregularities in the surface. Secondly, the scale is strictly linear in theory and remarkably so in practice, thus the first 8 cm. of the recording plate was calibrated by means of the H^+ group and also by means of the lines O , OH , OH_2 , OH_3 and the mass scale found to be linear to 1 in 10,000.¹ A third advantage claimed is that owing to the particular arrangement of the fields the lines produced are symmetrical, so that those of widely different intensity can be directly compared by measuring their optical centres.

On the other hand, as a means of estimating the relative abundance of isotopes a method depending on velocity selection is clearly less suitable than one, such as that used by the writer,² which makes an energy selection, for the following reason. In the ordinary discharge the energy of an ion depends upon its place of origin and subsequent path before reaching the cathode, so that if in the gas one isotope A is r times as abundant as another isotope B, then in the same small range of energy, wherever this is selected, there will be r times as many A ions as B ions. In other words the relative distribution of intensity along the parabolas of isotopes is identical, and our selection, one parallel to the OY axis (Fig. 4, p. 26) is the best possible.³ On the other hand, velocity selection means selection along a straight line through the origin O so that for this to give a correct ratio also, a further assumption must be made, that the distribution along the parabolas is uniform, which for any considerable difference of mass is clearly inadmissible. As an extreme illustration, if the velocity selected is the maximum detectable velocity of the lighter isotope no effects will be obtained at all from the heavier one, however abundant it may be.

The possibility of this source of error was realized in the method of intermittent exposures, and precautions taken to minimize it. It will not be serious in elements of high mass and may be neglected in estimates such as those, admittedly rough, of the isotopes of tellurium.⁴

It is a fortunate and most important fact that the apparatus of Bainbridge differs so fundamentally in principle from that used by the writer, for this ensures that the chance of both instruments reproducing the same experimental error is a very remote one. A great many elements have been examined by Bainbridge with his velocity selector apparatus, all of which had been previously investigated by means of the first or second mass-spectrograph. It is satisfactory that with very few exceptions, such as the spurious abundance of certain isotopes of Zn and Ge, all the results previously announced have been confirmed. It is of interest to note that the most im-

¹ Bainbridge, *Phys. Rev.*, 42, 3, 1932.

² V. p. 40.

³ V. p. 50.

⁴ Bainbridge, *Phys. Rev.*, 39, 1021, 1932.

portant advances achieved, namely the corrections in Zn and Ge, the discovery of new isotopes in Te and the measurements of the isotopic weights of H^2 and Be^9 resulted from more efficient methods of production of the rays rather than from higher resolving power in their analysis.

86. The Mass-Spectrometer.—Smythe and Mattauch¹ have recently described an instrument under this name by which mass rays can be analysed without the use of magnetic fields. The analysis depends upon a special type of velocity filter described by Smythe in 1926.² The principle of this is that if the rays pass successively through two identical alternating fields all but those having certain velocities can be removed. These velocities can be selected by altering the distance apart and the frequency of the alternations, the distance apart of the centres of the fields being such that a particle having the specified velocity enters the second field when the phase is opposite to that in which it entered the first. Fig. 23 shows the

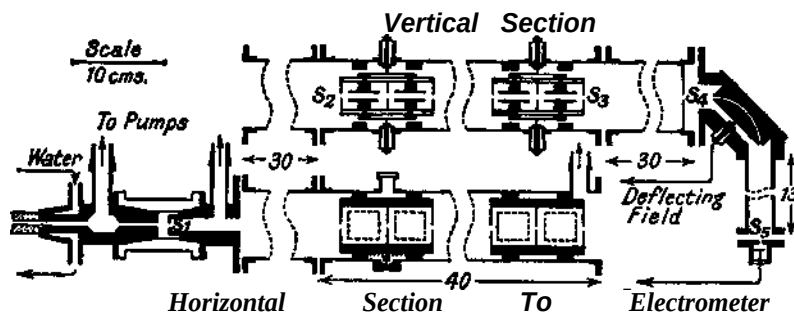


FIG. 23.—Diagram of the Mass-Spectrometer.

arrangement of the apparatus. Rays produced in a discharge tube emerge from the slit S_1 and pass through the collimating slit S_2 and then through the condensers forming the filter as indicated. The alternating field applied to the filter is supplied by a crystal-controlled oscillator with suitable amplifying system. The filtered beam is analysed by the deflecting electric field and peaks in the spectrum produced are detected by a collecting plate and electrometer at slit S_6 .

Because of the fact that a symmetry not anticipated in the theory was introduced in the construction for mechanical reasons, the apparatus transmits some other velocities besides those desired introducing complications into the mass-spectrum which is produced. Alterations in the design to avoid this difficulty are planned. The device has already been used to compare the intensities of the effects produced by the molecules of oxygen and its rare isotopes.

¹ Smythe and Mattauch, *Phys. Rev.*, 40, 429, 1932.

² Smythe, *Phys. Rev.*, 28, 1275, 1926.

CHAPTER IX

PHOTOMETRY OF MASS-SPECTRA

87. Methods of Determining the Relative Abundance of Isotopes.—The determination of the relative abundance of the isotopes of a complex element is of fundamental importance¹ and in addition affords a means of determining its chemical atomic weight by purely physical means. The most direct and general method is by some form of mass-ray analysis. The first quantitative measurements of the kind were made by Sir J. J. Thomson² who brought the parabolas, given by different particles, one after another to a parabolic slit behind which was a Faraday cylinder. The relative abundance was given by measuring the total charge entering the cylinder during a standard interval of time, the conditions of the discharge being taken as constant. Dempster³ used much the same device and was the first to obtain measurements of the relative abundances of isotopes by its means.

The writer⁴ considered the possibility of applying the electrical charge method to the second mass-spectrograph by an arrangement in which two Faraday cylinders collected the charges carried by the separate beams of two isotopic mass lines at the same time. This device eliminates the fundamental difficulty of obtaining a constant source, for the relative currents carried can be compared by a null method. For a variety of reasons it was, however, more convenient to continue to photograph the mass-spectra and to work out a means of measuring abundance by means of photometry. The methods by which this has been done will be described in this chapter.

88. Photographic Plates suitable for Mass-ray Analysis.—The earliest application of photographic plates to detect positive rays has already been noted.⁵ It was obvious from the first that their sensitivity to the rays bore little relation to their sensitivity to light. Sir J. J. Thomson realized that the penetrating power of the heavier rays was exceedingly small and that therefore the layer of sensitive silver salt should be as concentrated as possible. He endeavoured to make use of the old Daguerreotype process, which should give a

¹ V. p. 178.

² J. J. Thomson, *Rays of Positive Electricity*, 2nd ed., 120, 1921.

³ V. p. 69. ⁴ Aston, *Proc. Roy. Soc., A*, 126, 511, 1930. ⁵ V. p. 23.

maximum concentration, but without success. He records Schumann plates as being the most sensitive.¹

Comparative tests made in 1919 convinced the writer that of plates then commercially obtainable the type known as "Paget Half Tone" were the most convenient. They possess almost every merit possible for detecting and recording mass rays. Although highly sensitive to the rays they may be manipulated in bright yellow light without fear of fog. They have an extremely fine grain and owing to the thinness of their sensitized layer are fixed, washed and dried much more rapidly than ordinary plates. By far the larger number of experiments on mass-spectra have been made with the aid of plates of this type.

In 1922 efforts were made to give these plates the extreme sensitivity of Schumann plates by removing the gelatine by a method similar to that of Ducleaux and Jeantet.² The sensitivity of the "schumannized" plates made in this way was not altered much for light high-speed rays, but for heavy ones it was greatly improved and led to the discovery of large numbers of new isotopes. Schumannized plates deteriorate rapidly on keeping and their preparation and use entail serious technical difficulties, an account of which was given in 1925.³

For the measurements of high accuracy performed with the second mass-spectrograph uniformity was of paramount importance so that untreated Half Tone plates were used. Made with plate glass they were also used to develop the method of photometry to be described. During the latter work, however, an experimental type of Half Tone plate was tested.⁴ These new plates, which for convenience were referred to as "Q" plates, are coated with a fast-process emulsion of low gelatine content and were prepared in one of the Ilford Company's laboratories. They are from 5 to 7 times as sensitive to mass rays as the commercial Half Tone plates. They possess all the good qualities of the latter with a steeper and longer linear log range and appear to be much the best plates for general and accurate quantitative work with the mass-spectrograph.

These observations on plates refer to mass rays of energies ranging from 20 to 50 kilovolts. The blackening of photographic plates by rays of energies in the region of 1 to 2 kilovolts has been studied quantitatively by Bainbridge⁵ who gives curves for the opacity pro-

¹ *Rays of Positive Electricity*, 2nd ed., 4, 1921.

² Ducleaux and Jeantet, *J. de Physique*, 2, 154, 1921.

³ Aston, *Proc. Camb. Phil. Soc.*, 22, 548, 1925.

⁴ Aston, *Proc. Roy. Soc. A*, 132, 487, 1931.

⁵ *Jour. Franklin, Inst.*, 212, 489, 1931.

duced on Eastman X-Ray and Process plates by the impact of positive ions of the alkali metals. He comments on the extreme sensitivity of Schumann plates to rays of low velocity, but as they are unsuitable for photometry is unable to give any numerical data.

In order to link up his own observations with those of Bainbridge the writer has compared Q plates and Eastman X-Ray plates directly. Using rays of about 20 to 30 kilovolts energy it was found that Q plates were about 50 times as sensitive for heavy (mercury) rays and 250 times as sensitive for light (hydrogen) rays as Eastman X-Ray plates. A similar test of fresh Hilger Schumann plates showed that these might have a sensitivity as much as 20 times that of Q plates. The mass-spectra illustrated in Plate VII were all obtained with Schumann plates.

In conclusion it may be stated that, in the writer's opinion, for the detection of faint isotopes of heavy elements Schumann plates are unrivalled, though very troublesome to deal with. On the other hand, for all measurements, whether of mass or abundance, where uniformity is necessary some type of Half Tone plate, such as Q, is undoubtedly superior. There seems no theoretical reason why the sensitivity of this type of plate should not be improved while still retaining their insensitivity to light and other valuable properties. It is also possible that great sensitivity may be achieved by the incorporation of fluorescent material in the emulsion. Experiments are being carried out both by Ilford in England and by Eastman in America with these ends in view.

89. Methods of Photometry.—In 1929 the writer worked out methods by which the photographed spectra obtained with the second mass-spectrograph could be used to provide measurements of the relative abundance of isotopes. These have been since applied to determine the isotopic constitution of a large number of elements.¹ Standard Paget Half Tone plates were used and to ensure the best photometry these were coated on plate glass. In order to get a reasonable range of intensity with rays which only affect the surface of the plate a very strong and rapid developer must be used. Hence no attempt was made to ensure absolute uniformity of development by elaborate thermostatic control and mechanical mixing devices. What was aimed at was a series of operations so simple that they could be repeated again and again without serious variation. 20 c.c. of the hydroquinone developer recommended by the makers was mixed in a strong glass boiling-tube the length of the plate and closed with a rubber bung. When the exposed plate had been removed

¹ Aston, *Proc. Roy. Soc. A*, **126**, 611, 1930; **130**, 303, 1931; **132**, 487, 1931; **134**, 571, 1932.

from the mass-spectrograph this developer was warmed, usually by the fingers, to 20° C. exact to about 0.05°. The plate was dropped in and the tube was shaken longitudinally with considerable violence by hand for 90 seconds. The plate was then removed from the tube and rinsed in cold tap water for a few seconds after which it was fixed, washed and dried as usual. This period of development is rather less than that one would employ if searching for indications of the faintest lines, but it has the merit of leaving the background absolutely free from general fog and so simplifies the photometry. Comparisons are only made between lines on the same plate.

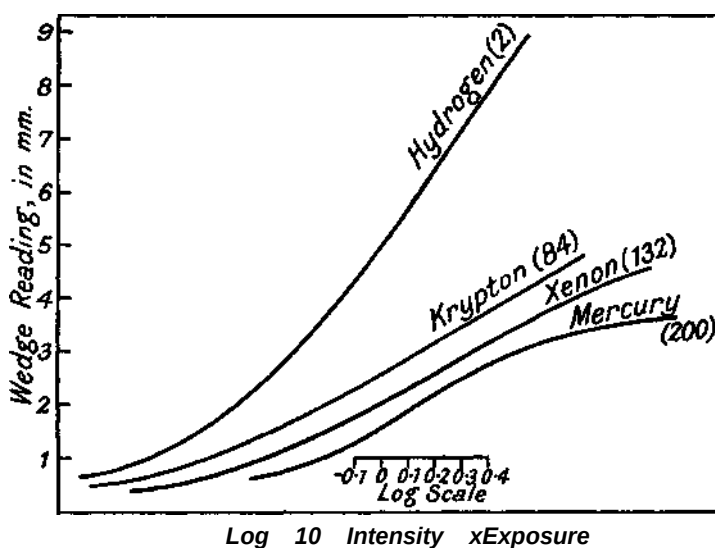


FIG. 24.—Curves illustrating the Photographic Effects of Mass Rays having the same Energy but different Mass. The Curves are only to be compared in general form, their positions relative to each other on the log scale have no significance.

The measurements were made with a microphotometer by balancing the opacities against a standard wedge by a null method. The opacity of mass-spectrum lines on the plates used is generally low so that the instrument was fitted with a pair of Ilford wedges having the low contact density graduation of 0.39 per cm. Even with these the readings were usually less than 5 mm. For actual measurement it was decided to take the peak value read on the wedge, using a moderate slit width to give high sensitivity and to diminish the grain effect. The slit corresponded to 0.08 mm. on the surface of the plate.

The relation between the total quantity of rays deduced by methods to be described and the wedge readings of peak values is indicated by the curves shown in Fig. 24 which are plotted from results obtained

with the hydrogen molecule and the atoms of krypton, xenon and mercury. The potential on the electric plates was 320 volts in each case, corresponding to rays of about 38 kilovolts. The exact forms of the curves vary with every plate, but these are typical.

The effect of the different penetration is very clearly indicated. The highly penetrating hydrogen particles do not give a linear log law until a fair density has been reached, but after that the curve is linear and shows no sign of change of slope. The data for this curve are very rough. For the krypton more accurate figures are available. It is closely linear for a considerable range of wedge reading. Xenon has a shorter linear range and the slope of the curve soon falls off. With mercury, which is the least penetrating of all, the increase in opacity falls off so soon that accurate deductions from wedge readings are only available over a very short range.

Having decided on the quantity to be measured, namely the peak values of the opacity of, say, two lines due to isotopes A and B, in order to connect it with the relative abundance of A and B we must make certain assumptions. The first and most important is that the ratio we wish to measure, the relative abundance of A and B, is a true invariant, and will be completely unaffected by experimental conditions. The evidence for this is overwhelming. The second assumption is that the photographic effect of A will be indistinguishable from that of B. This is approximate only, but since the masses of isotopes only differ by a few per cent, and their atoms have identical energies it is unlikely to lead to serious error in heavy elements. The third assumption is that the photographic effect will depend on the total number of particles striking the plate and not on the time they take to do so. In other words, with a constant source, if an exposure of R minutes with isotope B gives an effect identical with one of 1 minute with A we assume that the ratio of abundance of A to B is R. This is, of course, not strictly true of light quanta, but it seems sufficiently so for our purpose in the case of electrons and positive rays, and results so far have justified its validity.

90. Correction for position of Lines.—From the position of the plate in the mass-spectrograph it is clear that the width of the lines will vary with their position, so that if peak values are used to measure intensities a correction will have to be applied when comparing lines some distance apart. In order to obtain a value for this the theoretical width of the image given by standard slits was worked out by a graphical method, perfect focussing being assumed, and plotted against the distance from the fiducial spot. The extreme variation was about 2 to 1 over the whole plate and was very nearly linear over the range employed. This variation is so similar to that

of the dispersion factor that, to the accuracy expected of photometry, the relations between the actual line intensities of a group of isotopes may be treated as constant over a reasonable range of the plate. The numerical correction is roughly 1.5 times the percentage difference in mass, e.g. the true relative abundance of Kr^{86} as compared with Kr^{84} will be 3.5 per cent, greater than that indicated by its line intensity derived from the peak value of opacity. Results indicate that imperfect focussing, which cannot be corrected for, gives rise to variations as great as those due to inequalities in the photographic emulsion, and there seems little doubt that really good measurements will only be obtained by taking account of the line as a whole by an electrical method. To do this photometrically seems impracticable.

91. Method of Intermittent Exposures.—The most formidable obstacle in the way of starting an investigation of the photometry of mass-spectra is the problem of the constant source. Although, as will be seen, it is just possible, under particularly favourable conditions, to maintain a discharge approximately constant for several minutes, this is usually far from being the case, so that in the preliminary work it was essential that this source of uncertainty should be eliminated as far as possible. For this purpose two experimental conditions could be turned to advantage. The particular form of spherical discharge tube used was known to give very uniform distribution along the electric spectrum, and the resolution of the mass-spectrograph was so high that a change in the electric field of $\frac{1}{2}$ per cent, gave lines well separated. It was possible therefore to move a fine to an independent position on the plate without serious alteration in its intensity.

The actual way this was applied is indicated in Fig. 25. *G* is a large wheel with its circumference accurately divided in degrees; it is fitted with two radial arms which can be set at any desired angle to each other. The wheel is rotated at a constant speed of about one revolution in 15 seconds by a gramophone motor. As the arms revolve they engage alternately with the rocking reversing switch S_1 which applies the potential of the cell *C* first in one direction and then in the other, through the potentiometer R_2 , where it is reduced to a suitable small value, to the ends of the resistance R_1 placed in the circuit maintaining the high potential on the + and — plates of the mass-spectrograph. Hence instead of a single line at position corresponding to the standard voltage 320 volts we now get two lines, one each side of this position, near enough to be strictly comparable, peaks of which correspond to a ratio of exposures determined by the angle of the rotating arms. Changes in the condition of the discharge will have been minimized by breaking two long exposures into a very large number of intercalated ones. After one spectrum has been taken

the hand switch S_2 is reversed and an exactly similar one taken. The mean value of these should, at least theoretically, eliminate the small change in intensity due to slightly different voltage.

In the first experiments the simpler arrangement shown on the right of the diagram was used. Here the rotating arms merely opened and closed the switch S which was tripped by hand after each spectrum had been completed. This gave reasonably consistent results, and as the changes in intensity with small alterations of potential could not be foretold exactly, and the random error due to lack of uniformity in the photographic plate was large, it was only when work had proceeded for a long time that suspicion arose that the changes

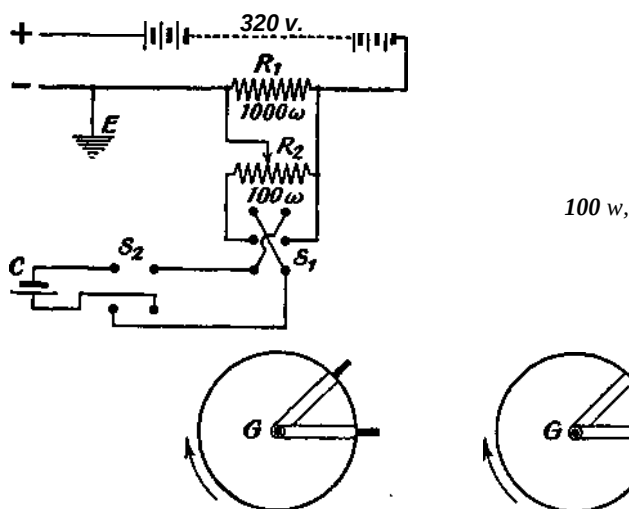


FIG. 25.—Diagram of connections used in the Method of Intermittent Exposures.

were not only greater than had been expected but not consistent with the variations in the hardness of the discharge. A careful study of the lines under a lens then revealed the fact that those formed after make showed slightly but unmistakably different characters and shapes from those formed after break of the disturbing circuit. Earth shielding of the moving mechanism failed to remedy this, so one was driven to adopt the more complex but entirely symmetrical arrangement.

92. Experiments with Krypton.—In the choice of an element for preliminary work one was guided by several considerations. It was essential that it should work well in the discharge tube. In order to make best use of the valuable fixed scale provided by nature it should have many isotopes with a large range of abundance. Finally its isotopes must differ by over 1 per cent, in mass so that the method

of intermittent exposures could be applied. Krypton satisfies all these conditions remarkably well. Its extreme rarity is no objection since the quantity used up is infinitesimal.

It is not necessary to describe the very large number of trials made with the arms of the rotating contact maker set at various ratios, 1 to 2, 1 to 3, 1 to 4, etc. It soon became evident that owing to the large random error due to inequalities in the surface of the photographic plate consistent numerical results could only be obtained by taking a mean of many spectra on the same plate. Six or seven were used as a rule. These indicated the range of opacity over which the log law could be trusted and enabled a curve such as that shown in Fig. 24 to be drawn. Such curves will not be identical for different plates but are of the same general form.

The measure of the fundamental ratio between the two strongest isotopes Kr^{84} and Kr^{86} was now undertaken by a method which virtually eliminates photometric error. Previous results showed that to obtain approximate equality between the reduced 84 line and the 86 fine the contact angles would have to be set at 3.6 to 1. With this setting the mean of seven spectra showed a difference of only 0.02 mm. wedge reading. The effect of the penumbra of neighbouring lines had to be allowed for and this was done by plotting the contour of typical lines and calculating their stray effect at different distances. When this correction had been introduced it was found that the ratio of the intensities of the lines was 3.53. Several interpolations on the log curve of other spectra had given ratios approximating to this, and a very good plate of six spectra taken with ratio 2 to 1 gave a corrected log difference 0.547, an identical result. Taking 3.53 as the ratio of intensity of the lines and correcting for the different positions of the two lines on the plate we get the final figure 3.41 for the relative abundance of these isotopes. This is probably within 2 or 3 per cent, of the true value.

The relative abundance of Kr^{83} , Kr^{82} and Kr^{80} were then computed in a similar manner. That of the faintest isotope Kr^{78} could only be obtained very roughly. The following table gives the results obtained by photometry of krypton mass-spectra :

KRYPTON RESULTS

Mass number of isotopes	78	80	82	83	84	86
Log reciprocal line intensity	2.083	1.336	0.668	0.676	0	0.547
Relative abundance $\text{Kr}^{84} =$	0.74	4.31	20.75	20.75		
Percentage abundance .	0.42	2.45	11.79	11.79	56.85	16.70

Knowing the masses of each isotope these figures enable the mean atomic weight on the physical scale to be fixed. As however the difference in packing fraction between isotopes is exceedingly small, sufficient accuracy is obtained by calculating the " mean mass number " 83.857 from the percentage composition and correcting this for the mean packing fraction—8.8 per 10,000. This gives a mean atomic weight on the physical scale of 83.783. If we assume the difference¹ between this and the chemical scale to be 2×10^{-4} the chemical atomic weight of krypton is $83.76(7) \pm 002$.

93. Experimental Error.—In evaluating the absolute ratio of abundance of isotopes the error may be of two kinds. One which may be called systematic is due to failure to fix the *scale* on which the ratios are measured through inconstancy of the source of error in timing. This clearly vanishes for fines of equal intensity and will be greatest when the ratio is high. The other is a purely random one due to inequality of the plate, focussing, etc., and will be just as high for equality as any other ratio. It is minimized by using the steepest part of the curve and can be reduced by taking a large number of observations. The photometer method is unfortunately very unsuitable for measuring large ratios of abundance. That between Kr^{84} and Ear^{78} has been arrived at by a series of ratios made possible by the occurrence of intermediate lines. The error is thus cumulative but even so the accuracy is far beyond any to be hoped for from a direct comparison of the lines.

In calculating atomic weights from mass-spectra the matter takes on an entirely different aspect. Here we are interested in the position on the mass scale of the centre of gravity of the group of lines which may be termed the " mean mass number." The effect of the systematic error on this will disappear for any symmetrical group of lines, and the larger the number of isotopes present on each side of the mean the more their random errors may be expected to cancel. Hence the percentage error per unit of mass number will compare very favourably with that of the most accurate ratios of abundance, large errors in the abundance of rare isotopes being automatically compensated for by the very fact of that rarity. In order to estimate the probable error in atomic weight the effect due to abundance and position of each line has to be considered separately.

The experience obtained during the experiments on krypton was of great value in extending the work to other elements. In the case of heavy complex elements, such as tin and mercury, the method of intermittent exposures could not be used, for the resolution of the apparatus was not sufficient. Instead the discharge was run as

¹ V. p. 189.

uniformly as possible and numerous exposures of different lengths made. From these, owing to the large number and range of abundance of the isotopes, it was possible to obtain calibration curves, as shown in Fig. 24, from which the best mean values could be deduced.

The determination of the values of the six main isotopes of mercury was of great importance. These form an approximate progression, a natural scale of abundance, and since the lines of this element appear on nearly all mass-spectra obtained by the discharge tube they can be used as a comparison scale for obtaining fair values of abundance for any other elements, such as tungsten, osmium, etc., of approximately the same mass.

As a method of determination of chemical atomic weights photometry of mass-spectra is clearly at its worst for light elements, for its error will be roughly a fixed fraction of the unit of mass. In addition with isotopes, as in lithium, so different in mass it is unsafe to conclude that particles of the same energy will affect the photographic plate equally. In the region of mercury the three sources of uncertainty due to packing fraction, change of scale and relative abundance have about the same value, each about 1 part in 10,000. Here the method will compare favourably with the best chemical ones and has obvious advantages from the fact that, in general, purity is of no importance, and the quantity of material required is usually only a fraction of a milligramme.

PART III

THE ELEMENTS AND THEIR ISOTOPES

CHAPTER X

INTRODUCTION, HYDROGEN, GROUPS 0, I AND II

Introduction.

In this part of the book the results obtained by the experimental methods described in Part II are stated for each individual element. The properties dealt with are purely nuclear, namely the isotopic constitution of the element and the isotopic weights of each species of atom in it. The latter will always be the weight of the neutral atom expressed on the physical scale $O^{16} = 16$. As regards the relative abundance of the isotopes this will be given in the form of percentages in multiple elements, but when only two isotopes are present, as in complex elements of odd atomic number, for greater convenience the ratio of their relative abundance will be used. There are no purely nuclear properties suitable for classification, so that in consideration of the fact that the methods of production of the mass rays of elements depend largely on their chemical properties they will be grouped together in the usual chemical way.

It has been suggested more than once by chemists that negative electricity should be treated as a chemical element with the electron as its atom. Such an element would correspond to an atomic number — 1 and mass number 0. On analogous principles the recently discovered neutron, if we take the view that it is a nucleus consisting of a single proton and a single electron, would be the atom of an element of atomic number 0 and mass number 1. It is, however, more usual to start the periodic table with hydrogen.

1. *Hydrogen.*

Hydrogen, the lightest of all chemical elements, has naturally played a predominant part in the development of mass-spectrum analysis. Derived from the water in the glass walls of the tube, and from other compounds, it is invariably present in the normal discharge, and the effects of its atom and molecule on the fluorescent screen were in fact the first phenomena observed in positive ray analysis. Since, with

beams of ordinary intensity, these two bodies are the only ones giving fluorescent effects easily discernable visually, they are, and are likely to remain, of indispensable value in testing and developing apparatus for analysis.¹ It is hardly necessary to state that no positively charged particle has been observed of smaller mass than the hydrogen atom, though a band effect may be produced at mass 0.5 which is due to abnormal conditions.²

Hydrogen behaves in the discharge like an electronegative element in that its nucleus tends to capture two electrons to form a negatively charged atomic ray H^- . The parabola due to negatively charged hydrogen will be clearly seen in Plate I.

Two positively charged molecules H_2 and H_3 usually occur, but in very disproportionate degree. The former gives the brightest line found in the ordinary low-pressure discharge, but the latter is usually barely distinguishable. Sir J. J. Thomson discovered that gas rich in H_3 could be produced by bombarding certain substances, such as solid KOH, with cathode rays.

Compared with the nuclei of ordinary atoms that of hydrogen, consisting of a single proton uncombined with negative electricity, is abnormally heavy. The divergence from the whole-number rule, amounting as it does to nearly 1 per cent., was easily detectable during the early work with the first mass-spectrograph. By the method of bracketing it was shown in 1920 that the chemical atomic weight 1.008 was in fact the weight of its atom.³ Costa, repeating these bracketing experiments with higher precision, arrived at the value 1.0079 for the weight of the hydrogen atom.

Accurate determinations of the packing fraction of hydrogen were made with the second mass-spectrograph.⁴

The hydrogen molecule was compared with the helium atom by Method III⁶ and measured against the known ratio $H:H_2$. The voltages applied were approximately in the ratio 2 : 1004, so that the H_2 line was on the heavy side of each doublet. The difference between the packing fractions of hydrogen and helium is the sum of the two intervals corrected for the mass of the electron. The intervals of mass came out on three plates to be 73.7, 73.6, 73.9, mean 73.73. From this must be subtracted the correction for the electron which in this particular case amounts to $\frac{1}{4} m_0 = 1.35 \times 10^{-4}$, whence we get 72.4 as the excess of the packing fraction of hydrogen over that of helium. The value of the latter is shown below to be 5.4, hence the packing fraction of hydrogen is 77.8, and therefore its mass 1.00778. This figure is virtually identical with the best determinations of its chemical

¹ V. p. 46.

² V. p. 60.

³ V. p. 50.

⁴ Aston, *Proc. Roy. Soc., A*, 115, 502, 1927.

⁵ V. p. 81.

atomic weight and in consequence, when the two isotopes of oxygen were discovered, with the resulting difference between the physical and chemical scales, Birge and Menzel¹ pointed out that to bring the results of the mass-spectrograph and those of the chemists into accord hydrogen must contain heavier isotopes. A search was carried out by Urey Brickwedde and Murphy² who were able to show by optical methods that at least one, the isotope of mass 2, did exist and could be concentrated considerably by distillation. The abundance of H^2 in ordinary hydrogen was first, erroneously, estimated to be 1 in 4000, enough to account for the discrepancy in atomic weights. Bleakney³ by mass-spectrum measurements of the proportions of different molecules present at very low pressures confirmed the existence of H^2 but estimated its abundance roughly at 1 in 30,000. The great rarity of H^2 has since been confirmed by the investigations of Hardy, Barker and Dennison⁴ on the infra-red spectrum of H^2C1 . Nineteen lines in band H^2C1^{35} and seventeen in band H^2C1^{37} were measured and the abundance estimated to be 1 in 35,000.

The packing fraction of H^2 , which is clearly of the greatest interest in connection with the structure of its nucleus, has been measured by Bainbridge⁵ who by means of his precision apparatus⁶ determined the interval, in units of mass, between the line of helium and that of the triatomic molecule $H^1H^1H^2$ obtained from the discharge in hydrogen enriched by distillation. Some of the spectra used are reproduced in Plate VII. Assuming the writer's value 400216 for helium, Bainbridge calculates the isotopic weight of H^2 to be 201351 ± 0.00018 , and its packing fraction to be 67.5. Estimates from optical work on the infra-red spectrum of H^2C1 already noted⁴ give a mass 2.01367 in reasonable agreement with this.

The most careful search has failed to disclose any other isotopes of hydrogen so that if we assume the later estimates for the abundance of H^2 the mean mass number of the element on the physical scale should be 1.00781. The most probable value of its chemical atomic weight from chemical and density results is given by Birge⁷ as 1.00777 ± 0.00002 . These figures give a difference of scale of only 0.4×10^{-4} as against 2.2×10^{-4} deduced from Mecke's measurements on the oxygen isotopes. This is a serious discrepancy and the difficulty

¹ Birge and Menzel, *Phys. Rev.*, 37, 1669, 1931.

² Urey Brickwedde and Murphy, *Phys. Rev.*, 40, 1, 1932; 39, 164, 1932.

³ Bleakney, *Phys. Rev.*, 41, 32, 1932.

⁴ Hardy, Barker and Dennison, *Phys. Rev.*, 42, 279, 1932.

⁵ Bainbridge, *Phys. Rev.*, 41, 115; 42, 1, 1932.

⁶ V. p. 85.

⁷ Birge, *Phys. Rev. Suppl.*, 1, 1, 1929; *Phys. Rev.*, 35, 1015, 1930.

of accounting for it has only been heightened by the recent re-determination of the hydrogen-helium ratio.

As had been suggested¹ the most reliable method of measuring this is by the direct comparison of the lines H_2 and He^{++} on a mass-spectrum. Bainbridge has now succeeded in doing this,² obtaining doublets shown in Plate VII. His measurements give for the isotopic weight of H^1 1.007775 ($He = 4.00216$), exactly confirming the value previously obtained by the writer, so that any allowance on the physical side can only fall on the helium-oxygen ratio which is very unlikely to be in error by as much as 1.8×10^{-4} . It must be concluded that the discrepancy between the isotopic weights and atomic weights of hydrogen and oxygen is at present unaccountable and further work upon the matter is desirable.

GROUP 0

The Inert Oases.

The gaseous nature and non-chemical properties of this group of elements render them particularly favourable to analysis by the ordinary discharge-tube methods. In consequence they have been essential in the development of mass-spectrum analysis and have been more completely studied than any other group. Thus neon, as has been described, was the first non-radioactive element shown to exhibit isotopy, and krypton with its six isotopes, the first multiple element observed, has been used as the standard group for the development of mass-spectrum photometry. All exhibit the property of multiple ionization which has been of such notable help in accurately plotting the physical mass scale.

2. *Helium.*

Early in his work with positive rays Sir J. J. Thomson noticed how easy it was to obtain a parabola corresponding to mass 4 both visually and photographically even with the smallest traces of helium present in the discharge tube. In this way he was able to show that the element was liberated from many substances by bombardment with cathode rays.³ Although the merest trace of helium will record its first-order line on a mass-spectrum it is only quite recently that its second-order line due to doubly charged helium, the well-known alpha ray of radioactivity, has been observed,⁴ and used v.s. to check the hydrogen-helium ratio of mass.

All attempts have failed so far to prove the presence of another

¹ Aston, *Nature*, **130**, 21, 1932.

² Bainbridge, *Phys. Rev.*, **43**, 103, 1933.

³ J. J. Thomson, *Rays of Positive Electricity*, 2nd ed., 191, 1921.

⁴ Aston, *Nature*, **130**, 21, 1932.

isotope. Some observations made in 1920 (since found capable of alternative explanation) suggested that a body of mass 3 was present in atomic nuclei and a careful search for atoms of this mass in helium from Canadian gas wells was made with the first mass-spectrograph,¹ but without success. The evidence of a helium of mass 5 is equally negative. A line at mass 5 does occur on mass-spectra taken with helium, but this seems certainly due to the abnormal compound $\text{HeH}^{1,2}$.

The atom of helium was the first to have its mass fixed with precision by means of the second mass-spectrograph. It was compared by Method III with the doubly charged oxygen atom O^{++} using the known ratio $\text{C}^{++} : \text{C}^+$ as a measure. For this purpose voltages roughly 242 and 362 were applied to the plates, bringing C^{++} and He into close approximation on one spectrum and C^+ and O^{++} together on the other. The packing fraction of helium will be measured by the difference between these intervals. The mean of four measurements gave 5.2. This must be corrected by the addition of $m_0/24$ so that the packing fraction of helium is 5.4 and its mass 400216. When allowances are made for change of scale this figure agrees reasonably well with those made from density determinations.

Helium is of all elements the most likely to be truly simple. Even if ordinary atmospheric and naturally occurring helium is not, it may be regarded as fairly certain that helium directly derived from radioactive material would be. Partly on this account it has been suggested as the best standard of atomic weight as it would give a scale which could be, theoretically, used both for physical and chemical measurements. On the other hand, its inert properties make it very unsuitable for a chemical unit.

10. Neon.

A full account of the early work on neon has already been given in Chapter IV. A faint line at 21 was noticed in the mass-spectra then obtained which suggested a third isotope. When it was realized that such an effect might be caused by an abnormal hydride it was considered safer to drop the figure from the tables until more definite evidence of its cause was available. In 1928 Hogness and Kvalnes³ working under conditions unfavourable to the formation of a hydride obtained conclusive evidence of the occurrence of Ne^{21} .

The first determination of the packing fractions of the two principal isotopes of neon was made with the second mass-spectrograph.⁴ The more abundant isotope Ne^{20} was compared with O by means of the

¹ Aston, *Phil. Mag.*, 45, 935, 1923. ^a V., p. 163.

³ Hogness and Kvalnes, *Phys. Rev.*, 32, 942, 1928.

⁴ Aston, *Proc. Roy. Soc. A*, 115, 487, 1927,

ratio $\text{CH}_8 : \text{C}$. The mean of three very consistent measurements of these intervals indicated that Ne^{20} has a practically negligible packing fraction 0.2 and a mass 20.0004. Ne^{22} was compared with Ne^{20} by the ratio $\text{CH} : \text{C}$. The numerical difference between these ratios is too large for accurate work, neither were the plates good. The mean results, a packing fraction 2.2 and mass 22.0048 are only to be regarded as provisional.

Bainbridge^x has recently measured the masses by an entirely different method, using the instrument described in Chapter VIII. As a mean of ten different measurements of the line Ne^{20} against lines of known mass he gives the value $19.99671 + 0.0009$ which corresponds to a packing fraction of -0.16 . By comparing doubly charged Ne^{22} with Ne^{20++} and C^+ and its hydrides on five spectra he obtains the value 21.99473 ± 0.00087 giving a packing fraction of -0.24 . As Bainbridge points out, his results agree better than the earlier ones with recent observations on atomic disintegrations, but the correspondence is not quite satisfactory.

The ratio of abundance of Ne^{20} to Ne^{22} has not been determined photometrically. The large difference of mass would be against the reliability of the method. Burton and Bartlett,² using a Dempster apparatus, estimated it as approximately 10, a value which was subsequently supported by the work of Hogness and Kvalnes already referred to. The latter estimated the abundance of Ne^{21} as 2 per cent, of the whole. This appears to be too high, for some recent measurements by Bainbridge (privately communicated) using photometry of the second-order lines, a method which eliminates the hydride contamination, show Ne^{22} to be 15 times as abundant as Ne^{21} . From the data available we may assume the most probable percentage abundance to be roughly

Mass number.	.	.	.	20	21	22
Abundance.	.	.	.	90.4	0.6	90

This is in good agreement with the value of the atomic weight on the chemical scale 20.182 deduced from the latest determination of density.³

18. Argon.

Argon was one of the first elements analysed by its mass-spectrum. As expected from the chemical atomic weight, it gave a very strong first-order line at 40. Second- and third-order lines at 20 and 13 1/3 were observed and owing to the position of the latter in the C_x group

¹ Bainbridge, *Phys. Rev.*, 43, 424, 1933.

² Burton and Bartlett, *Phys. Rev.*, 31, 22, 1928.

³ Baxter, *Jour. Amer. Chem. Soc.*, 50, 603, 1928.

of reference lines the mass of A^{40} could be fixed with unusual precision and certainty. It worked out to be a whole number within 1 part in 1000 and since the density atomic weight was then accepted to be 39.9 search was made for a lighter isotope. This was found to be 36, a very faint line. Spectra obtained with argon are shown in Plate III.

Determinations of the packing fractions have been made with the second mass-spectrograph.¹ The principal isotope was first measured against CO_2 by means of the approximate ratio $P:PH_3$. Better results were obtained from its second-order line using the more exact ratio $A^{40++}:O, CH_3:C$. The mean value for the packing fraction is — 7.2, giving a mass 39.971. This figure is supported by the later measurements of Bainbridge² who states a provisional value of 39.9724.

Experiments with isotope 36 were troublesome owing to its extreme faintness. It was measured by the approximate series $A^{36}:A^{40}:CO_2$. The measurements gave a packing fraction — 6.6 and a mass 35.976, but this needs confirmation.

No accurate measurement of the ratio of the abundance of the isotopes of argon has been made. During the experiments on the packing fractions the proportion of A^{36} was estimated to be less than 1 per cent. A calculation from the most reliable value 39.943 of its density atomic weight on the chemical scale suggest a ratio of about 160.

36. *Krypton.*

This was the first element shown to be highly complex. Its sixfold group of lines, reproduced in the second and third orders were the most striking phenomena disclosed in the early work with the first mass-spectrograph. One of the spectra then obtained is shown in Plate III. The proof that the isotopes had whole-number masses was easy, for their second-order lines could be compared with argon, already measured, and those of the third order with CO . On account of the fact that its mass-spectrum is very easy to produce and its lines have a good range of intensity free from possible contamination by compounds it was chosen as the standard group for mass-spectrum photometry. In consequence the data available for krypton are unusually complete and accurate. Measurements of high accuracy on its lines were made by means of the second mass-spectrograph. Some of the results then obtained are reproduced in Plate VI. Its position on the mass scale was best fixed by comparing the second-order line of its heaviest isotope at 43 with CO_2 by means of the known ratio $Br^{79}:Br^{81}$. The mean of measurements on three plates gave for its packing factor — 8.2, mass 85.929. This result was checked by a

¹ Aston, *Proc. Roy. Soc. A*, 115, 487, 1927.

² Bainbridge, *Phys. Rev.*, 43, 424, 1933.

comparison of the first-order line of Kr^{86} with the second-order line of the lightest isotope of mercury (Spectrum VIII) by means of the known ratio $\text{CH} : \text{CH}_3$ which, taking the value of mercury given below, gives identical agreement. The five even isotopes of krypton form an ideal subject for the series shift of two units. The six spectra shown (Spectrum XI) are all double spectra taken with the same voltage ratio, but with exposures suited to particular pairs of lines. The measurements show to an order of accuracy probably well within 1 in 10^4 that the masses of the isotopes of krypton form a perfectly uniform series. The determination of the common difference cannot be made with the same certainty, but it appears slightly greater than two units. An experiment with a series shift of one unit showed that the odd isotope Kr^{83} fell into the same series. The packing fractions and masses of the isotopes of krypton are given in the table.

The methods of photometry by which the relative abundances of the isotopes of krypton were determined have been fully described in Chapter IX. The data given by the mass-spectra of krypton are as follows :

Mass number	78	80	82	83	84	86
Packing Fraction	- 9.4	- 91	- 8.8	- 8.7	- 8.5	- 8.2
Mass	77.926	79.926	81.927	82.927	83.928	85.929
Abundance	0.42	2.45	11.79	11.79	56.85	16.70

These figures give an Isotopic Moment of 0.87 and a mean mass number of 83.857.

The chemical atomic weight, calculated from the density, was estimated in 1901 by its discoverer, Sir William Ramsay, to be 82. More accurate work by Moore in 1908 gave 83.012 which was later recalculated by Watson at 82.92. When the krypton group was first photographed on a mass-spectrum it was seen to indicate a considerably higher value roughly estimated to be 83.5.¹ When the mean mass number given above is corrected for packing fractions and change of scale it gives an atomic weight for krypton on the chemical scale of 83.767. More work is projected on the density of krypton,² in the meanwhile the higher value 83.7 has been adopted on the International Table.

54. Xenon.

The first mass-spectrum of xenon indicated five isotopes, but it was feeble and indistinct and their mass numbers were estimated a unit too low.³ Soon after by the use of a richer specimen of heavy

¹ Aston, *Isotopes*, 1st ed., 114, 1922.

² V. Allen and Moore, *Jour. Amer. Chem. Soc.*, 53, 2512, 1931.

* Aston, *Phil Mag.*, 39, 623, 1920.

inert gases these figures were corrected and two more isotopes 128, 131 indicated. During the critical examination of the heavier constituents of air for element 86 ¹ faint effects were seen at 124, 126. These were later confirmed on the second mass-spectrograph during investigations on its packing fraction.² All nine isotopes of xenon will be seen in Plate VI.

By a fortunate chance this element can be compared with mercury with the highest certainty, for its line 134 can be photographed in its second order between the two third-order mercury lines 66.6 and 67.3, without its position being seriously disturbed by that of the weak mercury isotope 201. The mean of a large number of measurements of this bracket give a packing fraction 61 less than that of mercury. Hence, taking the value of mercury given below Xe¹³⁴ has a packing fraction — 5.3 and a mass 133.929. During these experiments the two doubtful isotopes of xenon 124, 126 were noted whenever sufficient exposure was given, and are confirmed beyond any reasonable doubt. A critical comparison of the masses of the isotopes of xenon by Method II has not yet been carried out, but direct measurement of the intervals between them shows no notable deviation, and for the present they may be taken as having the same packing fraction.

The relative abundance of the isotopes of xenon have been determined by photometry,³ but as the lines are too close together to use the method of intermittent exposures a large number of spectra were taken with different exposures and from them a curve such as that in Fig. 24 constructed. The percentage results were—

Mass number	. 124	126	128	129	130	131	132	134	136
Abundance.	. 008	008	2.30	27.13	418	20.67	26.45	10.31	8.79

These figures give for xenon the high isotopic moment of 1.71 and a mean mass number 131.35. After correcting for packing fraction and change of scale this gives an atomic weight on the chemical scale of 131.26, a value much higher than that in use at the time the photometric measurements were made, but identical with that deduced by Whytlaw-Gray, Patterson and Cawood from the density determined by a micro-balance.⁴

86. Radon, Actinon, Thoron.

No non-radioactive isotope corresponding to this atomic number is known. It is clear that if such a substance is capable of existence it should be present in the atmosphere, its mass number should be

¹ q.v. ² Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927.

³ *Ibid.*, **126**, 511, 1930.

⁴ Whytlaw-Gray, Patterson and Cawood, *Proc. Roy. Soc., A*, **134**, 7, 1931.

between 210 and 230 and its boiling point will be that of radon, namely — 65°C . A critical search was made for it in 1923.¹ Fourteen years before the late Sir James Dewar had collected in charcoal the least volatile fractions from 439 tons of liquid air. These residues were purified and fractionated in a long series of operations down to a volume of 0.02 c.c, which should have contained practically the whole of the unknown element if present. This was analysed in the first mass-spectrograph but failed to show any indication of lines in the region expected. From this result it was inferred that if a heavier inert gas exists in the atmosphere it is certainly not present to the extent of 1 in 10^{15} and probably not to the extent of 1 in 2×10^{16} parts by volume.

No mass-spectra have yet been obtained with the known radioactive isotopes. Actinon is certainly, and thoron probably, too rare for the purpose. Radon could indeed be used to give its mass line 222 by introducing it into the discharge, but so far this has not been done, for the practical reason that the mass-spectrograph would probably be ruined for further work owing to the radioactive contamination involved.

GROUP I

The Alkali Metals.

These strongly electropositive monovalent elements do not form volatile compounds suitable for use in the ordinary discharge. They are, however, very suitable for anode ray methods and it was by means of lithium salts that anode rays were discovered. The alkaline halides when sufficiently heated are excellent sources of anode rays, particularly when in the presence of suitable catalysts, as in the Kunsman type of electrode.²

3. *Lithium.*

This metal has received much attention owing to the fact that its rays are easily produced and offer some hope of separation of isotopes in a pure state. Its isotopic constitution was first demonstrated in 1921. The photograph showing the two parabolas of lithium then obtained by the writer from a heated anode³ is shown in Plate I. Thomson used a composite anode and Dempster, who confirmed the presence of Li^6 shortly afterwards,⁴ ionized the vapour of the metal itself.

The masses of such light nuclei as those of the isotopes of lithium

¹ Aston, *Proc. Roy. Soc. A*, **103**, 462, 1923.

² V. p. 71. ³ Aston and Thomson, *Nature*, **106**, 828, 1921.

⁴ Dempster, *Phys. Rev.*, **18**, 415, 1921.

are naturally of the greatest interest in connection with the theories of nuclear structure, and this interest has been intensified by the recent discovery that lithium disintegrates under the bombardment of swift protons.¹ They were shown to be greater than whole numbers when compared with the carbon line by means of the first mass-spectrograph.² The only precision measurements so far available are those of Costa made with a mass-spectrograph giving an accuracy of 1 in 3000.³ He used a composite anode arranged in such a way that after registering the lithium lines it could be moved away to allow the ordinary "gas" lines of the discharge to be photographed. In this way he compared Li^6 with the helium atom, which he assumed to have a mass exactly 4, and obtained the value 6.009. Correcting the value of He to that now measured directly⁴ we deduce for Li^6 a packing fraction of 20 and a mass 6012. For Li^7 Costa gives 7.012 in $N = 14.008$, which corresponds to a packing fraction of 17. The ratio of the masses of the Li isotopes has been estimated from measurements on optical spectra to be 1.04103 ± 0.00018 .⁵

Many experiments have been made to determine the ratio of abundance of Li^7 to Li^6 . The first made by Dempster,⁶ using his magnetic spectrograph, gave results indicating ratios so high as 37 and so low as 4.8 with means around 7-10, and are of little value. Morand,⁷ using a heated anode and measuring simultaneously the currents carried by Li^6 and Li^7 , arrived at the figure 14.9, a ratio agreeing well with the chemical atomic weight 6.94 on the assumption that the atoms had exact whole-number masses. The reliability of this result is, however, considerably reduced by the fact that Morand's apparatus was not capable of resolving the two atomic streams completely, so that the final figure was only obtained by indirect calculation.

Costa's masses given above combine with the chemical atomic weight 6.940 to give a ratio 12.9.

A detailed investigation on the subject has been recently made by Bainbridge⁸ who attributes the spurious variation in the ratio observed by Thomson and Dempster to effects of space charge. Bainbridge employed heated spodumene as his source and was able to achieve great constancy with it. He gives three figures 10.75, 11.28, 11.51 for the ratio of the currents carried by Li^7 and Li^6 concluding that the most probable value is 11.28 ± 0.07 . If we assume that

¹ Cockcroft and Walton, *Proc. Roy. Soc. A*, **136**, 619, 1932.

² Aston, *Phil. Mag.*, **47**, 393, 1924.

³ V. p. 72.

⁴ V. p. 103.

⁵ McKellar, *Phys. Rev.*, **43**, 215, 1933.

⁶ Dempster, *Phys. Rev.*, **18**, 415, 1921.

⁷ Morand, *Comptes Rendus*, **182**, 460, 1926 ; *Ann. de Physique*, **7**, 164, 1927.

⁸ Bainbridge, *Jour. Franklin Inst.*, **212**, 317, 1931.

perfect mixing takes place at the source, to get the relative abundance this must be multiplied by $1/Z$ to correct for the isotope effect

V 6

in free evaporation,¹ giving the final figure 12.187.

From photometry of the mass-spectra derived from a composite anode containing LiBr and Lil² the writer estimated the relative intensity of the beams at 11. This is only a rough value and it is impossible to say how far such an anode will exhibit the free evaporation effect.

It will be seen that all the recent direct physical measurements are in good agreement with each other and also with the indirect calculation from the atomic weight. It does not seem possible to accept the very much lower ratio of abundance 7.2 calculated from observations on band spectra.³ The atomic weight of lithium on the chemical scale worked out from Costa's masses and Bainbridge's ratio of abundance is 6.936 in good agreement with the International figure 6.940.

11. Sodium.

Like those of lithium the anode rays of sodium are easy to obtain. Its parabola is indicated in the picture of the lithium parabolas in Plate I. When examined with the first mass-spectrograph it gave one line only⁴ and was assumed to be simple of mass number 23. The very accurate analysis made by Bainbridge⁶ has confirmed this conclusion to an unusually high degree. Using rays from heated jadeite he was able to prove that mass numbers 21 and 25 could not be present to the extent of 1 in 3000, nor 22 to the extent of 1 in 800.

The packing fraction of sodium has not yet been measured directly, but the latest value of its chemical atomic weight 22.997 suggests that it is nearly zero, as is to be expected from the packing fraction curve.

19. Potassium.

Behaving similarly to sodium, anode rays of potassium are easy to produce and the effect due to a small quantity of this element is distinguishable in the early parabola photograph of lithium reproduced in Plate I. Its isotopes were first analysed by the first mass-spectrograph,⁶ and shown to have mass numbers 39 and 41, the former being

¹ V. p. 226.

² Aston, *Proc. Roy. Soc. A*, **134**, 574, 1932.

³ v. Wijk and v. Koeveringe, *Proc. Roy. Soc. A*, **132**, 98, 1931; Nakamura, *Nature*, **128**, 759, 1931.

⁴ Aston, *Phil. Mag.*, **42**, 436, 1921.

⁵ Bainbridge, *Jour. Franklin Inst.*, **212**, 317, 1931.

⁶ V. p. 65.

very much the more abundant. This result was confirmed and the relative abundance measured by Dempster ^x who estimated the ratio to be 18, which is in fair agreement with the chemical atomic weight 39.10. No other determinations of the ratio have been published, but as attempts to achieve direct separation of the isotopes of potassium by mass-ray analysis are now being made in more than one laboratory more definite figures will probably soon be available. No measurement of the packing fraction of potassium has yet been made.

Potassium has long been known to be feebly radioactive. It has recently been demonstrated ² that this property is due either to isotope 41 or to other undiscovered heavy isotopes. Bainbridge ³ has shown that these cannot be present in any appreciable amount.

37. *Rubidium.*

This element behaves similarly to potassium and was analysed into its two component isotopes 85 and 87 at the same time by adding rubidium chloride to the anode mixture.

The ratio of the abundance of the rubidium isotopes has been determined by the photometry of its mass-spectra. ⁴ The most probable ratio of Rb⁸⁵ to Rb⁸⁷ was found to be 3.0. The packing fraction has not been determined but is unlikely to differ much from that of Kr⁸⁸ which is — 8.2. Assuming this value and correcting to the chemical scale the atomic weight works out to be 85.43 ± 0.03 , in good agreement with the latest International one of 85.44.

Like potassium rubidium is radioactive, but no experiments have yet been carried out to discover which, if either, of its known isotopes is unstable.

55. *Cesium.*

When this element was first investigated ⁵ by a heated anode of caesium chloride, only one line appeared, corresponding to mass number 133, although the chemical atomic weight was 132.81. The simplicity of caesium was confirmed later to a high degree by Bainbridge ⁶ who used as a source of its rays a tantalum strip coated with pollucite. He quotes the percentages of hypothetical lighter components required to bring its atomic weight into agreement with the chemical value, and states: "No indication has been obtained of

¹ V. p. 70.

² V. p. 229.

³ Bainbridge, *Jour. Franklin Inst.*, **212**, 338, 1931.

⁴ Aston, *Proc. Roy. Soc. A*, **134**, 575, 1932.

⁵ Aston, *Phil. Mag.*, **42**, 436, 1921.

⁶ Bainbridge, *Phys. Rev.*, **36**, 1668, 1930.

any single one of the possible isotopes being present to even one-tenth of the above percentages."

As the only other obvious explanation of the low chemical weight would be an abnormal packing fraction of — 14.3 this quantity was measured directly by means of a special discharge tube by which the caesium line could be photographed between the lines 132 and 134 of xenon of which the packing fraction is known. No abnormality was found and the most probable packing fraction of caesium is $-5.0 \pm 2.^x$ This corresponds to an atomic weight on the chemical scale of 132.917 which suggests that the present value 132.81 is too low.

87. (*Eka-caesium*.)

Many efforts have been made in the past to demonstrate the existence of this element. The methods of mass-spectrum analysis were applied to the problem in 1929 by Bainbridge² who used a special form of Dempster magnetic spectrograph for the purpose, and critically examined the region round mass number 223. In his report, to which the reader is referred for an account of previous work on the subject, Bainbridge states : " Eka-caesium was not existent to an extent greater than 3.5×10^{-7} part of the caesium from pollucite or greater than 7.3×10^{-6} part of the caesium from lepidolite."

More recently Papish and Wainer³ have made a provisional claim to have detected element 87 in samarskite by X-ray analysis. This has been supported by the work of Barnes and Gibbs⁴ who by means of a Dempster apparatus have detected positive ions of mass (roughly) 220 in the sulphate of element 87 provided by Papish.

The Coinage Metals.

29. *Copper.*

The only data on this element were obtained with the first mass-spectrograph by means of anode rays.⁵ An anode of cuprous chloride, lithium iodide and rubidium chloride was used. The last salt was added to provide reference lines. The effects obtained from copper were faint, but conclusive, as both in intensity and position its lines appeared in accordance with statistical considerations.⁶ These lines are 63 and 65;⁷ they were measured against Rb^{85} on one side and

¹ Aston, *Proc. Roy. Soc. A*, **134**, 573, 1932.

² Bainbridge, *Phys. Rev.*, **34**, 752, 1929.

³ Papish and Wainer, *Jour. Amer. Chem. Soc.*, **53**, 3818, 1931.

⁴ Barnes and Gibbs, *Phys. Rev.*, **40**, 318, 1932.

⁵ Aston, *Phil. Mag.*, **47**, 395, 1924. ⁶ V. p. 175.

⁷ In *Nature*, July 7, 1923, Dempster described some results obtained with his apparatus which led him to the conclusion that copper had three isotopes

Fe⁵⁶ on the other, and show no measurable deviation from the whole-number rule. The ratio of their intensities was about 5 : 2 in reasonable agreement with the chemical atomic weight 63.57.

47. Silver.

This element was investigated at the same time as copper. An anode containing silver chloride and lithium iodide, gave a definite result, though the discharge was rather unsteady. Silver has two isotopes whose mass lines when measured against that of iodine have integral values 107 and 109. The first of these is slightly the brighter. Owing to the weight of accumulated statistical evidence in connection with the relation between odd atomic number and odd atomic weight and the exceptional trustworthiness of the work on the chemical atomic weight 107.880, this result might be described as a foregone conclusion.

19. Gold.

From statistical considerations and the fact that its chemical atomic weight is well authenticated, it is highly probable that gold consists of isotopes 197, 199 both isobaric with mercury, but so far it has not been found possible to obtain its mass-spectrum. The vapours of the chloride and of the chlorocarbonyl have been tried unsuccessfully in the discharge, and its compounds appear too unstable to use for anode rays.

GROUP II

The Metals of the Alkaline Earths.

This group of elements yield anode rays, but far less readily than the alkali metals. No success has followed from attempts to introduce into the discharge the few volatile organic compounds of them available. In consequence few accurate measurements have been obtained.

4. Beryllium.

As compared with other very light elements beryllium has given unusually scarce and unsatisfactory data. That its principal isotope had mass number 9 was shown by means of the parabola method by G. P. Thomson.¹ Later by means of accelerated anode rays applied to the first mass-spectrograph this fine was found to indicate a slight excess over an integer, but within the accuracy of experiment.² In all of even atomic weight. The relative intensities of these lines suggested that they were probably due not to copper but to zinc adventitiously present (V. Nature, Aug. 4, 1923).

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

² Aston, *Phil. Mag.*, **47**, 393, 1924.

each case rays from an anode containing beryllium fluoride were used, but the effects were feeble in intensity so that faint isotopes if present could not have been detected.

The exact mass of beryllium is of importance in connection with its remarkable property of yielding neutrons when bombarded with alpha rays.¹ It has only been measured very recently by Bainbridge² using Be Cl_2 as a source of ions. By comparing Be^9 with C^{12} by means of the ratio $\text{C} : \text{CH}_4$ he obtains a mass 9.0155 ± 0.0008 corresponding to the high positive packing fraction 17.2 very different from those of the other light even-numbered elements.³

The possibility of a lighter isotope of mass 8 is of great interest. Its existence is essential in the theory of the evolution of the elements put forward by Atkinson and Houtermans⁴ who suppose that it is capable of disintegration into two alpha particles, and indeed Lord Rayleigh⁵ has called attention to the fact that the normal beryl contains unexplainably large quantities of helium. Watson and Parker made a critical search for this isotope by analysis of the band spectra given by an arc between beryllium electrodes in an atmosphere of hydrogen at 6 cm. pressure.⁶ They claim to have found definite evidence of its existence to the amount of about 1 in 2000. Owing to the very crowded nature of the field searched the proof cannot be regarded as entirely conclusive, and so far it has not been confirmed.

12. Magnesium.

Magnesium was the first metal to be analysed by means of its anode rays. Dempster announced the discovery of its three isotopes in December, 1920.⁷ Its mass rays were obtained with anodes of two types. In the first experiments the heating coil was wound directly on a rod of magnesium, and the whole covered with a glass tube having a hole 3 mm. in diameter between the magnesium and the cathode to restrict the electron bombardment. Later an anode of the type illustrated in Fig. 17 was used. With both types three components with atomic weights 24, 25 and 26 were found. They appeared together as the magnesium was heated so as to vaporize slightly, and their atomic weights could be checked by comparison with rays at 28, probably due to occluded nitrogen, which is driven off before the rays of the metal appear. The relative proportions of the isotopes as indicated by the heights of their peaks on the curves

¹ Chadwick, *Proc. Roy. Soc., A*, **136**, 692, 1932.

² Bainbridge, *Phys. Rev.*, **43**, 367, 1933.

³ V. p. 168.

⁴ Atkinson and Houtermans, *Zeits. f. Physik.*, **54**, 664, 1929.

⁵ Rayleigh, *Nature*, **123**, 607, 1929.

⁶ Watson and Parker, *Phys. Rev.*, **37**, 167, 1931.

⁷ Dempster, *Science*, Dec. 10, 1920.

obtained varied somewhat in the earlier experiments. The curve given in Fig. 26 was made from observations with the later type of anode; it is the latest and probably the most reliable published.¹ It is drawn with the maximum of the lighter component exactly at 24, although its position was not compared in this case with the gas line at 28 to the accuracy indicated in the curve. The component at 24 is about 6·7 times as strong as the one at 25, while the latter is about 1·04 times as strong as the one at 26. These correspond to the following composition:

Mass number		24	25	26
Abundance		77·4	11·5	111

giving a mean mass number 24·336. The chemical atomic weight of magnesium is 24·32.

As Dempster's observations did not afford an accurate measurement of the masses of the isotopes, except relative to each other, the element was later investigated with the first mass-spectrograph by the method of accelerated anode rays.² An anode mixture containing the chloride was used and with some difficulty the line 24 was obtained and measured against Na²³. It showed no deviation from an integer. The effects were too feeble for the other lines to be seen. The lines of magnesium have not yet been examined with an instrument of high precision so no data are available on its packing fraction.

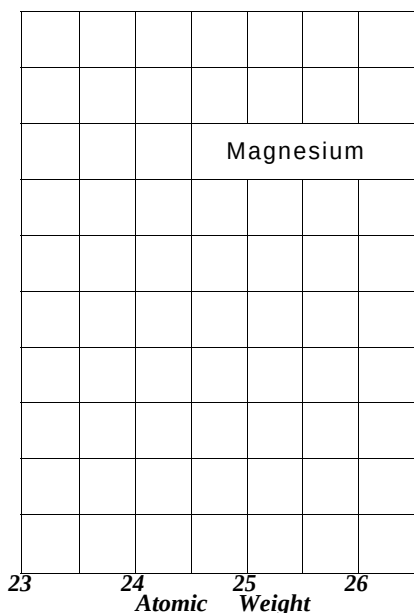


FIG. 26.—Curve for Magnesium.

20. Calcium.

This element was first investigated by Dempster who found that it behaved well in his later apparatus,³ showing a strong peak at 40 and a very weak one at 44. The masses of the two lines of calcium were compared by observing the potentials for the maxima. The accuracy with which the observations may be made is shown in Fig. 27. The centre of each line indicates the value taken as the maximum

¹ Dempster, *Phya. Rev.*, 18, 421, 1921. ² Aston, *Phil. Mag.*, 47, 393, 1924.

³ Dempster, *Phys. Rev.*, 20, 633, 1922.

and the length of the line indicates the estimated possible error in the setting. The first two lines show the comparison with K^{39} . The possibility of the line at 44 being due to CO_2 was tested by distilling the calcium in a vacuum, but the ratio of intensities of 70 to 1 previously found was not appreciably altered, so that we may conclude that calcium consists of two isotopes of mass numbers 40 and 44. The above ratio gives a mean mass number of 40.055. The chemical atomic weight is 40.07.

The mass of the calcium line 40 was more accurately measured by the application of accelerated anode rays to the first mass-spectrograph.¹ Calcium does not give anode rays at all readily. In some experiments the chloride was used, in others the fluoride, but in no case was the Ca^{40} line as strong as that of K^{39} although potassium was carefully excluded from the anode mixture. The second-order calcium line was detected at 20. The first- and second-order lines of

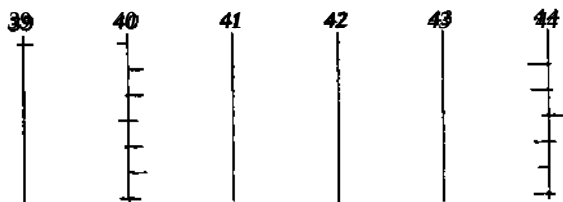


FIG. 27.—Comparison of Atomic Weights for Calcium.

calcium, both lines of potassium, and the strong single lines of sodium and aluminium could all be compared on the same spectrum and were found integral with one another within the error of experiment, that is 1 in 1000.

No determination has been made of the mass of Ca^{40} on an instrument of precision so its packing fraction is still uncertain.

38. Strontium.

In the first investigations of strontium by accelerated anode rays various halides were used, but only one line at 88 could be detected.² Further work revealed a fainter component 86.³ More recently the high resolving power of the second mass-spectrograph and improved conditions of vacuum enabled a more searching analysis to be made.⁴ Using an anode containing a mixture of SrI_2 and $LiBr$ the strong component 88 and weak companion 86 were confirmed and in addition a third isotope 87 was discovered. The relative abundances were

¹ Aston, *Phil. Mag.*, 47, 394, 1924.

² *Ibid.*, 47, 395, 1924.

³ *Ibid.*, 49, 1192, 1925.

⁴ Aston, *Proc. Roy. Soc. A*, 134, 573, 1932.

roughly estimated from the photometer readings and correspond to a composition :

Mass number		86	87	88
Abundance		10.0	6.6	83.4

The packing fraction of Sr^{86} has not been measured, but it is unlikely to be very different from that of Kr^{86} which is -8^*2 . If this is assumed, the atomic weight of strontium works out on the chemical scale to be 87.64 ± 0.06 in good agreement with the chemical value 87.63.

56. Barium.

The early results obtained from barium by accelerated anode rays using an anode of barium chloride and lithium bromide were misleading, only one line 138 being detected.¹ The explanation of this became clear when, by the use of the high resolving power of the second mass-spectrograph and very long exposures three more isotopes 135, 136, 137 were discovered.² These lines are faint and in ascending order of intensity so that with the imperfect resolution of the original instrument they were quite indistinguishable from a naturally graded penumbra of the much more intense line 138. The relative abundances of the isotope were measured photometrically giving the following results, for which however no great accuracy can be claimed.

Mass number	. . .	135	136	137	138
Abundance	. . .	5.9	8.9	111	74.0

A determination of the packing fraction of Ba^{138} was made by means of the special arrangement of the discharge tube described for caesium. The anode contained BaCl_2 and LiI and the comparison line used was that at 139 due to IC , which together with ICH and ICH_2 appeared strongly under these conditions. The resulting figure was -6.1 ± 2 . From this the atomic weight of barium works out on the chemical scale to be 137.43 in reasonable agreement with the accepted chemical value 137.36.

88. Radium.

No attempt has been made to get the mass-spectrum of radium. It may be expected to behave like barium and so be amenable to anode-ray treatment. There is every reason to conclude that radium is simple and of mass number 226. Its packing fraction can be calculated by radioactive data from that of uranium lead, its ultimate disintegration product.

¹ Aston, *Phil. Mag.*, **49**, 1192, 1925.

² Aston, *Proc. Roy. Soc. A.*, **134**, 573, 1932.

The Mercury Group.

30. Zinc.

This metal was first investigated by Dempster.¹ The results were at first inconsistent, but curves obtained from a calcium anode to which had been added a little zinc gave sharper bundles of rays and were regarded as satisfactory. The form of the curve is shown in Fig. 28.

The values for the mass numbers were obtained by direct comparison with the calcium line at 40 ; they indicated that zinc consisted

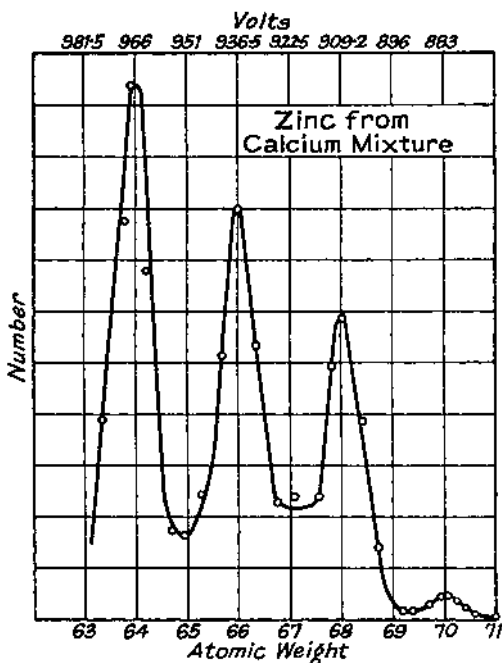


FIG. 28.—Dempster's Curve for Zinc.

of three strong isotopes 64, 66, 68 and a fourth faint one 70. The probability of an unresolved isotope 67 was suggested.

Early attempts to confirm this result on the first mass-spectrograph by the use of zinc methyl failed to show any zinc lines at all.² Later experiments with the second mass-spectrograph³ made it clear that the secret of obtaining strong zinc lines was to have nothing but the vapour of zinc methyl present. The presence of other elements more

¹ Dempster, *Phys. Rev.*, **20**, 633, 1922.

² Aston, *Phil. Mag.*, 45, 937, 1923.

³ Aston, *Proc. Roy. Soc. A*, **130**, 303, 1931.

easily ionized or capable, from any other cause, of carrying the current more easily seems to act adversely. Doubtless the many earlier failures to get zinc lines were largely due to the presence of mercury. The low ionization potential and abnormally great "current carrying" power of this element appear to enable it to suppress the mass-spectrum of zinc entirely, although the partial pressure of the latter is far the greater.

The mass-spectra obtained not only showed the lines found by Dempster, and confirmed that at 67, but there were in addition lines at 65 and 69, both stronger than that at 70. As these showed no variation in their intensity they were taken to be genuine isotopes and the relative abundances of the group worked out by the method of intermittent exposures, were found to agree exactly with the chemical atomic weight.

More recently, however, Bainbridge,¹ by the use of his high-power apparatus² and metallic zinc vapour as a source of ions, has obtained results which prove beyond question that isotopes 65 and 69 are not present to an appreciable extent, even compared with 70, in the mass rays of zinc. One of the spectra obtained by Bainbridge, is reproduced in Plate VI. It is clear that the lines 65 and 69 were due to the hydrides of the abundant isotopes 64 and 68. An inspection of the relative intensities of the lines shows that these are in exact accord with the assumption that a monohydride corresponding to 5.2 per cent, of each isotope was present. Correcting the original figures for this amount of hydride gives the following percentage abundance :

Mass number . . .	64	66	67	68	70
Abundance . . .	50.4	27.2	4.2	17.8	0.4

giving for zinc an isotopic moment 1.41 and a mean mass number 65.40.

The determination of the packing fraction of zinc was made possible by the fortunate occurrence of the higher carbon groups in the rays from the discharge through zinc methyl.

When the tube had been running for a long while with nothing but zinc methyl passing and had reached steady conditions, spectra obtained with fairly long exposures all showed not only the C₃ group, but, rather fainter, the C₄ group. In the former the line 39 C₈H₃ is the strongest, in the latter line 50 C₄H₂. Why these molecules appear when metallic compounds are used and why they are produced in these proportions, or indeed at all, in the discharge are problems worth a special research and need not be further discussed here. The importance in this work is that their identity seems beyond dispute, so

¹ Bainbridge, *Phys. Rev.*, 39, 847, 1932.

² V. p. 85.

that they provide the necessary standards for the determination of the packing fraction of zinc, and by good fortune the ratios 39 : 50 and 50 : 64 are near enough for that purpose.

In this way a provisional value of — 9.9 was found for Zn^{64} . Correcting for this and the change to the chemical scale we get for the atomic weight of zinc 65.33, rather lower than the accepted one 65.38.

48. *Cadmium.*

In sharp contrast to zinc and mercury, cadmium is very difficult to deal with in mass-ray analysis. After several failures its lines were first revealed by the first mass-spectrograph, using the method of accelerated anode rays.¹ With an anode of cadmium fluoride and lithium fluoride prolonged exposure yielded one mass-spectrum showing fairly satisfactory intensity and detail. This was fortunate, for cadmium is so complex an element and its lines so near the limit of resolution that without the enhanced resolving power given by the peculiar properties of schumannized plates it is doubtful if any reliable interpretation could have been made.

The spectrum shows a group of six isotopes. Very rough provisional estimates of their relative abundance are

Mass number	110	111	112	113	114	116
Abundance	14	12	24	10	35	5

which agree reasonably well with the chemical atomic weight 112.41.

The general resemblance of the group to that of tin was remarked and when methods of photometry had been worked out for the second mass-spectrograph every effort was made to apply these to cadmium. Its methyl compound, which was confidently expected to behave like that of zinc, proved entirely intractable,² so that no accurate data are available either for its packing fraction or the abundance of its isotopes. Further work on cadmium is now being undertaken by Bainbridge whose preliminary spectra show no marked differences from that described above.

80. *Mercury.*

This element has a unique position of importance in the technique of mass-spectra. As it is usually employed in the exhaustion and admission of gas in the apparatus for the ordinary discharge, and is particularly favourable to the production of mass rays it is extremely difficult to eliminate it from mass-spectra obtained in this way. This is fortunately neither necessary nor desirable in most cases, for it

¹ Aston, *Phil. Mag.*, 49, 1196, 1925.

² Aston, *Proc. Roy. Soc. A*, **130**, 302, 1931.

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 parabolas¹ enabled Sir J. J. Thomson 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, 661, 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. Study of the group showed the presence of a strong line at 202, a weak one at 204 and an unresolved band.² It was not until the second mass-spectrograph was working that the main lines were properly resolved and shown to be 198, 199, 200, 201, 202, 204.³ Several photographs of the second-order group of mercury are reproduced in Plate VI. Later a very rare component 196 was identified,⁴ and quite recently evidence of 197 and 203 in still smaller quantities has been obtained.⁵

The determination of the packing fraction of mercury⁶ is of unusual interest, for the element is in some respects the most important of all elements in work on the determination of the masses of atoms by their mass-spectra. Not only are its rays exceptionally easy to produce, but its unique series of multiply charged groups are to be taken gratefully as divisions naturally inscribed on the mass scale which connect the highest atomic masses with the lower ones without fear of accumulative error. During the present work the group could be distinguished even down to the sixth order. The accurate comparison between mercury and oxygen is of the highest importance so that it may be used as a sub-standard. This has not yet been done satisfactorily. A measurement of its packing fraction was obtained by comparing CO₂ with triply charged Hg¹⁹⁸ by means of the known ratio of the second- and third-order lines of mercury

¹ V. Plate I. ² Aston, *Phil. Mag.*, 39, 623, 1920.

³ Aston, *Nature*, **116**, 208, 1925. ⁴ *Ibid.*, **120**, 224, 1927.

⁵ *Ibid.*, **130**, 847, 1932.

⁶ Aston, *Proc. Roy. Soc. A*, **115**, 508, 1927.

themselves. This is by no means easy to do, for the potentials need be set very accurately to enable the two mercury groups to be clearly resolved, for, at the best, their interpolated lines can only differ by 1 in 400. Only one plate giving a good result has been obtained. On this the two intervals were indistinguishable. Hence, mercury would have the same packing fraction as CO_2 , namely 0.8, and the mass of Hg^{200} would be 200.016. Comparison of the mercury lines with one another fails to show any difference between their mass intervals and unity on the oxygen scale. They may all be taken to have the same packing fraction.

Mercury is also of importance in photometry. It is the heaviest element yielding mass rays easily and, as has already been noted, its group forms an invaluable natural reference scale of abundance for elements of similar weight. The curve of the photographic efficiency of its rays shown in Fig. 24 indicates that it is not particularly favourable to the method, and its lines are too close for the most reliable method, that of intermittent exposures, to be employed. Many spectra had therefore to be taken and the best mean values were as follows :¹

Mass number	196	197	198	199	200	201	202	203	204
Abundance .	0.10	(001)	9.89	16.45	23.77	13.67	29.27	(0006)	6.85

These correspond to an isotopic moment of 1.40 and a mean mass number of 200.63. The latter after correction gives an atomic weight on the chemical scale identical with that in use, 200.61.

The isotopic moment of mercury has peculiar interest, for it is the only one which has been determined experimentally by entirely different means.² The agreement is identical.

¹ Aston, *Proc. Roy. Soc. A*, **126**, 523, 1930.

² V. p. 227.

CHAPTER XI

GROUPS III, IV, AND V

GROUP III

5. *Boron.*

The very early discovery of the isotopic nature of boron is due to the fact that it forms a stable gaseous fluoride BF_3 which can be introduced into the discharge tube without difficulty. After a failure to obtain a result with boron hydride the fluoride was used mixed with COa .¹ Very complex and interesting spectra were obtained and it was remarked that the gas possessed an extraordinary power of resurrecting the spectra of gases which had been previously used in the discharge bulb, doubtless due to the chemical action of the fluorine liberated.

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 and 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 6 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 the lines 5 and 5.5 did not agree well with an atomic weight as high as 10.9, the value then in use, and the discrepancy might have been explained by the presence of a third isotope at 12. This would be masked by carbon, for it was not 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 60 for B^{12}F_2 . The line at 49 is very strong, but at 60 any

¹ Aston, *Phil. Mag.*, 40, 628, 1920.

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, and the more recent values of its atomic weight are in fair agreement with the results of the mass-spectrograph.

The packing fractions of both isotopes of boron were measured with the second mass-spectrograph.¹ As before, boron trifluoride was used to give the lines of the element.

The lighter isotope B^{10} was compared with O^{++} by the use of the known ratio $CH_3:C$. B^{11} was compared with C by the known ratio $C:CH$, which is sufficiently near for the purpose. The results so obtained were checked by comparing the ratio $B^{10}:B^{11}$ with that of $B^{11}:C$. Using the mass of C given below, the results of these three comparisons were in good agreement, and gave for B^{10} the packing fraction 13.5, mass 100135; and for B^{11} the packing fraction 10.0, mass 110110.

Valuable confirmation of the relative accuracy of these masses has been obtained from measurements of the band spectrum of boron oxide excited by active nitrogen.² The ratio of the masses of the boron isotopes calculated from the results of the mass-spectrograph given above is 1.09962 ± 0.00032 . The ratio calculated from the band spectrum is given as 1.09961 ± 0.00006 .

Among complex elements boron has the highest known "separability,"³ hence it is not surprising that the evidence for variation of atomic weight in naturally occurring boron seems stronger than for any other (non-radiogenic) element. Although Munro⁴ could detect no difference between European boron and that from sources in New Zealand, Briscoe and his co-workers⁵ give for the atomic weight of boron from three different sources: California 10.847; Tuscany 10.823 and Asia Minor 10.818.

The photometry of mass-spectra derived from boron trifluoride of unascertained but probably European origin⁶ gave a ratio of abundance of isotope 11 to isotope 10 of 3.85, not of high accuracy owing to the large correction for the position of the lines. This ratio must necessarily be too low as the photograph effect of the lighter isotope must certainly be enhanced by its greater velocity and penetrating power. The correction is not ascertainable, but if we make the rough assumption that it is proportional to the velocity the ratio will be 4.04 corresponding with an atomic weight on the chemical scale of 10.815, in good agreement with the international value 10.82.

¹ Aston, *Proc. Roy. Soc. A*, **115**, 502, 1927.

² Jenkins and McKellar, *Am. Phys. Soc. Meeting*, Dec, 1931.

³ V. p. 183. ⁴ Munro, *Trans. Ghem. Soc.*, **121**, 986, 1922.

⁵ Briscoe, *Jour. Chem. Soc.*, **127**, 696, 1925; *ibid.*, 70, 1926.

⁶ Aston, *Proc. Roy. Soc. A*, **132**, 490, 1931.

The ratio of the abundance of the boron isotopes has also been measured by means of band spectra. Elliott¹ from photometry of the bands of BO (Chilian boron) estimates it to be 3.63 ± 0.02 . On the other hand, from observations on the bands of BH Paton and Almy² give the much higher figure 4.86 ± 0.15 .

13. *Aluminium.*

From the close approximation of its chemical atomic weight to an integer and the rule concerning the isotopes of elements of odd atomic number aluminium was from the first expected to be simple.³ During some experiments on tellurium chloride with the first mass-spectrograph the chlorine liberated attacked the electrodes unmistakably. In fact, the slit in use was ruined by the corrosion. It is therefore perfectly certain that volatile aluminium chloride must have been present in quantity during the exposures. The indication of its presence was equally strong on the mass-spectra obtained. The line at 27, usually very much weaker than that at 28, was very intense, and its second-order line easily visible at 13.5. Furthermore, strong groups of lines appeared with their first units at 62 and 97. The intensities of the lines in these groups show that they are due to the mono- and dichlorides of bodies having masses 27 and 28. The latter may be an atom of Si²⁸ or a molecule of CO, but the only possible origin of the former is an atom of aluminium.

When a further attack on tellurium chloride was made with the second mass-spectrograph⁴ a strong line at 27 was obtained on a plate showing no trace of the C₂ group. It is therefore reasonably certain that the element consists mainly of atoms of mass number 27.

Measurements of the packing fraction of aluminium have not yet been feasible owing to the extreme difficulty of eliminating the line C₂H₃ and at the same time retaining reference lines suitable. This is unfortunate on account of the very remarkable behaviour of its nucleus under the bombardment of alpha rays.

31. *Gallium.*

After a failure to obtain the lines of the element from its volatile chloride it was successfully analysed by the method of accelerated anode rays,⁵ the anode containing the fluoride made by the action of hydrofluoric acid on the pure hydride. The results were faint but

¹ Elliott, *Nature*, **126**, 845, 1930.

² Paton and Almy, *Phys. Rev.*, **37**, 1710, 1931.

³ Aston, *Phil. Mag.*, **40**, 633, 1920.

⁴ Aston, *Proc. Roy. Soc. A*, **132**, 494, 1931.

⁵ Aston, *Phil. Mag.*, **47**, 397, 1924.

gave satisfactory proof that the element consists of two components of mass number 69 and 71. The intensities of the two lines agree well with the chemical atomic weight 69-72. No accurate data are yet available for gallium.

49. *Indium.*

The mass rays of this element were obtained from an anode containing its fluoride which had been prepared from a sample of metallic indium.¹ The mass spectrum shows one line only at 115. This, when measured against I^{127} and Cs^{133} shows no deviation from the whole-number rule. This line has not been obtained so far of sufficient intensity to rule out the possibility of a small percentage of a second isotope suggested by its chemical atomic weight 114-8.

81. *Thallium.*

Positive evidence of the constitution of this element has only recently been obtained by means of its slightly unstable ethyl compound.² Exactly as expected, its mass numbers are 203 and 205, the heavier predominating as in the case of rhenium. The presence of the lines of mercury in suitable strength made the determination of the relative abundance and the packing fraction unusually easy. The ratio works out to be 2-40 and the packing fraction roughly 1.8 ± 2 , which, after the necessary corrections, gives

Atomic weight of thallium = 204.41 ± 0.03 ,

in excellent agreement with Honigschmid's value 204.39 now in use, and supporting this rather than the more recent figure 204-34 given by Briscoe, Kikuchi and Peel.³

The Bare Earth Elements.

The only results on this interesting family of elements have been obtained by accelerated anode rays and are meagre and unsatisfactory. The complete lack of information on the constitution of the heavier members forms the most serious gap in our knowledge of the periodic table of isotopes. The first mass-spectrograph had insufficient resolving power and several recent attempts to apply the second to the problem have all failed.

21. *Scandium.*

This is the only one of the rare earths for which satisfactory data

¹ Aston, *Phil. Mag.*, 49, 1192, 1925.

² Aston, *Proc. Roy. Soc. A*, 134, 571, 1932.

³ Briscoe, Kikuchi and Peel, *Proc. Roy. Soc. A*, 133, 440, 1931.

have been obtained. In the early work * an anode containing the fluoride was used and only one line at 45 was detected, but as it was very faint this did not disprove the presence of isotopes suggested by the chemical atomic weight of 45.1. Using the second mass-spectrograph, these experiments have been repeated² with an anode consisting of scandium fluoride, from the same sample as that originally used, and a little potassium bromide. The scandium line was obtained at once and by exposing for over 1 hour the intensity of this was increased to such a value that any other isotope present to the extent of 3 per cent, could have been detected. None was, which proves that scandium is simple to that degree.

The packing fraction of Sc^{46} has not been determined accurately, but from its position on the plate relative to K^{41} it is certain that these two are integral with each other to 1 in 2000. The chance that both these atoms have entirely abnormal masses need hardly be considered, hence a mass of 45.1 for scandium is inadmissible. From the curve the most probable packing fraction for Sc^{45} is — 7, and, if we assume this and correct for change of scale, we get

Atomic weight of scandium — 44.96 ± 0.05 ,

which suggests that the chemical value 45.1 needs revision.

39. *Yttrium.*

The only results on this element were obtained with the first mass-spectrograph with an anode containing the fluoride.³ The mass-spectrum showed one line only 89 which when compared with that of iodine appeared integral within experimental error. Its chemical atomic weight 88.92 is in good agreement with the idea that yttrium is a simple element.

57. *Lanthanum.*

This element was investigated by means of its bromide, which when mixed with lithium bromide worked smoothly as an anode. With an exposure of half an hour a single line 139 was obtained of such a strength as to make it reasonably certain that lanthanum was a simple element as its chemical atomic weight 138.90 would lead one to expect.⁴

58. *Cerium.*

Results from cerium were obtained by the use of its bromide. Its strongest line is 140. On the best spectra then obtained a second

¹ Aston, *Phil. Mag.*, 47, 396, 1924.

² Aston, *Proc. Roy. Soc. A*, **134**, 571, 1932.

•Aston, *Phil. Mag.*, 47, 398, 1924.

⁴ *Ibid.*, **49**, 1191, 1925.

fainter component 142 could be seen. The intensity of this is in fair accord with the chemical atomic weight 140-13.*

59. *Praseodymium.*

An anode containing the pure bromide gave a single line at 141. This evidence combined with the chemical atomic weight 140-92 make it reasonably certain that praseodymium is a simple element of mass number 141.¹

60. *Neodymium.*

Results were obtained from the bromide only with extreme difficulty. Under good experimental conditions and using the most highly sensitive schumannized plates three lines 142, 144, 146 were detected not differing much in intensity. There was a faint possible component at 145, but this is doubtful.¹

61. (*Illinium*), 62. *Samarium*, 63. *Europium*, 64. *Gadolinium*,
65. *Terbium*, 66. *Dysprosium*, 61. *Holmium*, 68. *Erbium*,
69. *Thulium*, 10. *Ytterbium*, 11. *Lutecium*.

No definite information on the isotopic constitution of these elements is yet available. With the first mass-spectrograph by means of accelerated rays from an anode containing erbium bromide faint results were obtained in the region 164-167 which suggested that erbium was complex, but attempts to repeat this analysis with the second mass-spectrograph have failed so far.

GROUP IV

6. *Carbon.*

The importance of this element in the development of mass-ray analysis can hardly be overestimated. It is invariably present in the ordinary discharge and its lines and those of its compounds were from the first used as reference fines. There was no positive indication whatever to suppose it to be otherwise than simple and of mass number 12,² and the very close integral relation between its chemical atomic weight and that of oxygen strongly supported this conclusion. Carbon and its hydrides form well-marked groups of reference lines which were of the greatest value in developing the scale of mass. The first which may be called the d group contains five lines, 12—C, 13—CH, 14—CH₂, 15—CH₃, 16—CH₄ and is well shown in Spectrum V, Plate III, and also under greater power of resolution in Spectrum I, Plate VI. The second or C₂ group 24—C₂, 25—C₂H—also appears frequently, derived from hydrocarbons in the wax and grease used in the joints

¹ Aston, *Phil. Mag.*, 49, 1191, 1925.

² *Ibid.*, 39, 619, 1920.

of the apparatus. It can be seen in Spectra I, **II**, **III**, Plate **III**. The higher groups C_8 and C_4 appear, for some obscure reason, when metallic methyls and carbonyls are present.

The accurate evaluation of the packing fraction of carbon is of importance on account of its use as a sub-standard of mass. It can be measured in two ways. The more direct is to make use of the approximate geometrical progression $O^{++} : C : OH_2$. The technical objection to this is that the water line is only well developed in a new discharge bulb and its intensity is very difficult to gauge. On the other hand, the comparison is very favourable, for the square of the unknown is involved and any uncertainty in the mass of hydrogen only enters in the second order. The mass of carbon can also be measured in terms of hydrogen and oxygen by means of the close doublet O, CH_4 seen in Spectrum I, Plate VI. Both types of measurement are consistent with a packing fraction for carbon of 3.0 and mass 120036.¹

The discovery of the isotopes of oxygen introduced a discrepancy in atomic weights which suggested the existence of a higher isotope of carbon and in 1929 King and Birge² from observations on the band spectra of C_2 were able to announce the discovery of a rare isotope C^{13} . The presence of this was later confirmed by Birge³ in the band spectra of CO and CN. In their later report⁴ from which the illustration, Plate VIII, is taken King and Birge conclude that the masses of the two isotopes of carbon are integrally related to 1 part in 10,000 and estimate the ratio of abundance as 400. The latter is admittedly uncertain as the strength of the isotopic band relative to the primary one may depend upon the excitation conditions. Thus they found that it appeared many times less abundant in the arc than in the furnace. In addition it has been observed⁶ that in some R and N types of stars the $C^{12}C^{13}$ band is quite abnormally intense, though it seems highly improbable that the ratio should be altogether different to that found in terrestrial carbon.

Taking the estimate of abundance given above and correcting to the chemical scale the atomic weight of carbon works out at 12.0037 in reasonable agreement with the chemical value 12.0025.

14. Silicon.

It is obvious that there is always a possibility of this element appearing in rays from ordinary discharge bulbs on account of its occurrence in the glass walls. The presence of its principal isotopes

¹ Aston, *Proc. Roy. Soc. A*, **115**, 487, 1927.

² *Phys. Rev.*, **30**, 825, 1927. ³ *Nature*, **124**, 13, 1929.

⁴ *Astrophys. Jour.*, **72**, 251, 1930.

⁵ Sanford, *Pub. Ast. Soc. of Pacific*, **41**, 271, 1929.

28 and 29 was first demonstrated in spectra taken with BF_3 ¹ and reproduced in Plate IV. The reasoning was as follows:

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 then accepted as 28.3 indicated that this could not 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 presence of a silicon of mass number 30 was suggested by the lines 30, 49, 68, 87, but the possibilities of hydrogen compounds made this inconclusive. Valuable confirmation of this isotope was afforded later by the analysis of the band spectra of silicon nitride by MuUiken,² and conclusive proof was afforded by mass-spectra obtained during the work on zirconium,³ when all three lines of silicon were obtained under circumstances which precluded the presence of hydrides.

Recently during some work with BF_3 using the second mass-spectrograph⁴ on some of the spectra a faint line could be seen corresponding to a mass of $9\frac{1}{3}$. This was clearly Si^{28+++} and provided an opportunity for obtaining a provisional value of the packing fraction of Si^{28} . Its first- and second-order lines at 28 and 14 are invariably invalidated by the presence of CO , CH_2 , N and other bodies. The new third-order line, on the other hand, does not suffer from this disability, and moreover, is so close to F^{++} (9.5), a body the mass

¹ Aston, *Phil. Mag.*, 40, 628, 1920.

² Mulliken, *Nature*, **113**, 423; 489, 1924.

³ Aston, *Phil. Mag.*, 49, 1198, 1925.

⁴ Aston, *Proc. Roy. Soc. A*, **132**, 491, 1931.

of which is known with great certainty, that approximate determinations can be made by direct measurement. The best values so far show that the packing fraction of Si^{28} lies between -6.1 and -7.2 and can be taken provisionally as -6.5 ± 1.0 .

No accurate measurements of the relative abundance of the isotopes of silicon are available. The relation between Si^{29} and Si^{30} is roughly 2:1, but the comparison between them and Si^{28} will be difficult owing to the probable presence of other bodies of that mass number. The International chemical atomic weight is at present 28.06, though a more recent revision gives 28.103 ± 0.003 .¹ It would appear that the most probable rough estimate agreeing with the known facts is

Mass number	.	.	.	.	.	28	29	30
Abundance	.	.	.	.	.	91	6	3

32. *Germanium.*

The first investigation of germanium was made by accelerated anode rays using a compound resulting from the action of HF on the oxide. Three lines were detected of mass numbers 70, 72, 74.² A more searching analysis was made by means of the second mass-spectrograph using the volatile germanium tetra-ethyl in the ordinary discharge. This showed eight lines 70 ... 77 of which 71, 75 and 77 were weak, but all were assumed to be isotopes. The relative intensities of the group were determined by the photometry of mass-spectra obtained by the use of the more volatile and convenient methyl compound.³ More recently Bainbridge⁴ has examined germanium by means of its bromide and iodide. The spectra he has obtained, one of which is reproduced in Plate VI, make it quite clear that most, if not all, the effect given by the alkyl compounds at 71, 75, 77 are due to hydrides, and that the existence of these isotopes must be regarded as doubtful. A re-examination of the writer's results has shown that they are not incompatible with this conclusion, and although the fit is not so good as in the case of zinc, it is possible by applying a correction for the presence of about 7.3 per cent, monohydride to obtain the following figures for the relative abundance :

Mass number	.	70	(71)	72	73	74	(75)	76	(77)
Abundance	.	21.2	?	27.3	7.9	37.1	?	6.5	?

which give an isotopic moment of 1.48 and a mean mass number of 72.66.

¹ Weatherell and Brundage, *Jour. Amer. Chem. Assoc.*, 54, 3932, 1932.

² Aston, *Phil. Mag.*, 47, 394, 1924.

³ Aston, *Proc. Roy. Soc. A*, 132, 495, 1931. ⁴ Not yet published.

The packing fraction of germanium has not been measured. If we assume it to be between those of zinc and selenium and correct for change of scale the atomic weight works out to be 72.58 in excellent agreement with the chemical value 72.60.

50. Tin.

This very complex element was first investigated by means of its volatile tetrachloride. The vapour of this compound attacks the tap grease used in the apparatus which makes it difficult to deal with. The lines of some of the isotopes of tin were actually visible on one mass-spectrum, but could not be identified at the time.¹ The use of the tetramethyl gave much better results and enabled seven isotopes to be identified by the first mass-spectrograph.² The spectra then obtained had a peculiar interest owing to the accidental occurrence of xenon in the discharge. The fine of the monomethyl of the most abundant isotope of tin $\text{Sn}^{120}\text{CH}_3$, with its mass number 135, should have appeared symmetrically placed between the lines Xe^{134} and Xe^{136} . Actually the asymmetry was so marked that it was estimated that the difference of packing effect in the nuclei of the isotopes of tin and xenon must amount to at least 0.2 unit of atomic weight. This seemed theoretically very improbable, but the evidence then available appeared, and on re-examination still appears, quite conclusive.

When the greater resolving power of the second mass-spectrograph was available tin was again examined by means of its tetramethyl and no less than eleven isotopes identified.³ Spectrum X, Plate V, shows the mass fines of tin and also the comparison between the groups of tin monomethyl and xenon made at the same time.

The lines of xenon 132, 134, 136 and of tin monomethyl 133, 135 are widely resolved and form a perfectly uniform series. It is therefore quite certain that the conclusions from the former observations were erroneous. The error appears to be due to the accumulation of several effects, an unequal spreading of the xenon lines, which were stronger than the fine at 135, and an optical illusion possibly accentuated by the properties of the schumannized plate. It is a striking example of the danger of drawing any conclusions whatever from the apparent positions of lines not clearly resolved.

Measurements with the comparator show perfect symmetry in the brackets so that allowance for the excess due to CH_8 makes the packing fraction of tin 2.0 less than that of xenon. Taking the value — 5.3 for xenon Sn^{120} has a packing fraction — 7.3 and a mass 119.912. As

i Aston, *Phil. Mag.*, 42, 141, 1921.

² *Ibid.*, 45, 939, 1923.

³ Aston, *Proc. Roy. Soc., A*, 115, 506, 1927.

far as measurements have been made among the tin lines themselves it appears that they all have the same packing fraction.

The relative abundance of the isotopes of tin has been measured by photometry¹ giving the following percentages :

Mass number	.	.	112	114	115	116	117	118
Abundance	.	.	107	0.74	0.44	1419	9.81	21.48
Mass number	.	.	119	120	121	122	124	
Abundance	.	.	1102	2704	2.96	503	619	

The order of these intensities fortunately excludes the possibility of any of the fines being entirely due to hydrides which are evidently not present in serious quantity. The figures correspond to the very high isotopic moment of 1.77. The mean mass number is 118.82 which when corrected for packing fraction and change of scale gives a chemical atomic weight of 118.71, virtually identical with the International one 118.70.

82. Lead.

As has been pointed out in Chapter II, lead is unique among the elements in being formed in workable quantities on the earth as the result of radioactive disintegrations. The isotopic constitution of radiogenic lead will obviously depend upon the particular process of its evolution, and indeed the first proof of the existence of isotopes was the fact that lead originating from uranium had a smaller atomic weight than that originating from thorium. The vast bulk of terrestrial lead does not fall into the same category. It has a constant isotopic constitution and atomic weight. It is in every respect a perfectly ordinary complex element, and may be conveniently treated as such. The radiogenic leads, on the other hand, are definitely abnormal and their constitution is of the greatest importance both in the problems of radioactivity and of geologic time.

Ordinary Lead.—Although some faint and incompletely resolved effects were obtained by the use of finely divided metallic lead in the work on accelerated anode rays,² the only method so far producing rays of adequate strength is the discharge through its volatile tetramethyl. Rays produced in this way were first successfully analysed with the second mass-spectrograph. Owing to the evolution of hydrogen in the discharge, and the presence of this in the camera, the mass-spectra obtained were ill defined but showed the three principal isotopes 206, 207, 208 roughly in proportions 4, 3, 7.³

A much more satisfactory analysis has since been made⁴ using

¹ Aston, *Proc. Roy. Soc. A*, **130**, 303, 1931.

² Aston, *Phil Mag.*, 49, 1198, 1925. ³ Aston, *Nature*, **120**, 224, 1927.

⁴ Aston, *Proc. Roy. Soc. A*, **140**, 535, 1933.

better vacuum technique for reducing the pressure in the camera. **Five new** isotopes were indicated, one **of** which Pb^{104} had already been **independently** discovered by Schuler and Jones from their work on hyperfine structure.¹ The resolution of the lines of lead in the second mass-spectrograph is not sufficient to allow of the method of intermittent exposures, but fortunately lead methyl, if sufficiently pure, gives a remarkably steady discharge and consistent ratios of abundance can be obtained by taking a series of spectra with exposures of different periods. The following figures for abundance were obtained after correcting for the presence of 2.3 per cent, hydride.²

Mass number	. 203	204	205	206	207	208	209	210
Abundance	. 004	1.50	003	27.75	20.20	49.55	0.85	008

These figures give an isotopic moment 0.84 and a mean mass number 207.190. It was found impossible to determine the packing fractions of the isotopes of lead satisfactorily, but they are probably about 0 to + 1 so that the results are in fair accord with the International atomic weight 207.19.

Radiogenic Leads.—The problem of the isotopic constitution of the various leads found associated with radioactive minerals, which by their variation of atomic weight gave so convincing a proof of isotopy, was one of the greatest interest. As soon as a method of analysis of ordinary lead had been found efforts were made to obtain the necessary methyl compounds of these rare leads. The first successful analysis was made with a tetramethyl of a uranium lead from Norwegian Broggerite prepared at the Geophysical Laboratory, Washington.³ This was analysed with the second mass-spectrograph. The spectra were very faint and indistinct owing to the hydrogen in the camera, but lines 206, 207, 208 were visible and their intensities were estimated photometrically to be 100, 10.7, 4.5.⁴ At the time there was no reason to suppose that these could be affected by the presence of a hydride, so the percentages were worked out to be 86.8, 9.3, 3.9.

The presence and intensity of line 207 were of fundamental interest. As it was much stronger than line 208 it could not be due to the presence of ordinary lead as an impurity, for in ordinary lead 208 is more than twice as strong as 207, neither could it be the product of the disintegration **of** radium **or** thorium. There was, therefore, every reason to identify it as the end product of the only other known disintegration series, namely that of actinium. This settles the mass numbers of all the members **of** the series, that of protactinium being 231. Assuming

¹ Schiiler and Jones, *Naturwiss.*, 20, **171**, 1932.

² V. p. 60.

³ Piggot, *Jour. Acad. Sci.*, 18, 269, 1928.

⁴ Aston, *Nature*, **123**, **313**, **1929**.

the ratio of 100 : 7 for the number of atoms of uranium lead to actinium lead Lord Rutherford¹ was able to work out the period of actino-uranium, the parent of the actinium series, and an isotope of uranium, to be 4.2×10^8 years, and deduce other important cosmical conclusions.

Further knowledge of the isotopic constitution of radiogenic leads was highly desirable in connection with the problems of geologic time and the origin of actinium. Dr. A. v. Grosse, who was particularly interested in the latter problem, undertook the preparation of the methyls of a variety of rare radiogenic leads and these have recently been analysed successfully by means of the second mass-spectrograph.² The work was troublesome as it was found necessary to set up a fresh discharge tube for each sample, but with the aid of better vacuum technique clean, sharp mass-spectra were obtained and it was found possible to measure, and correct for, hydride present in the following way.

A sample of pure thorite lead gave lines 206, 207, 208, 209 with relative intensities finally established at 4.9, 1.5, 100, 2.3. Now Pb^{209} is known to exist only to a small extent in ordinary lead so it is at once obvious from the intensities of lines 206 and 207 that any effect at 209 caused by the presence of traces of ordinary lead in the sample can be neglected. On purely theoretical grounds the presence of Pb^{209} in so pure a thorium lead is extremely improbable and this conclusion is fortunately supported by evidence from the mass-spectrum itself. There is corresponding to the line 208, another very strong line 223 due to PbCH_3 , but no trace of an effect at 224 could be detected. This is negative evidence which in the case of isotopes is always the most conclusive. It is therefore quite safe to conclude that under the particular experimental conditions the discharge in lead methyl gives rise to a monohydride only and this to the extent of 2.3 per cent. It is admittedly unfortunate that any hydride at all is formed, but so long as every effort is made to ensure the closest agreement of experimental conditions it is possible to use this figure with considerable confidence. The following are descriptions of the leads examined and the results obtained after correction for 2-3 per cent, of hydride.

Katanga I. Lead from pitchblende, Katanga, Belgian Congo. Methyl prepared from chloride used by Honigschmid for his determination of the atomic weight (206.048).³

Katanga II. Extracted by Grosse and Kurbatow from Katanga pitchblende supplied by Mme Pierre Curie and Mme Irene Joliot-Curie. Atomic weight 20605.

¹ Rutherford, *ibid.*

² Aston, *Nature*, **129**, 649, 1932 ; *Proc. Roy. Soc., A*, **140**, 535, 1933.

³ Honigschmid and Birckenbach, *Ber. deut. chem. Ges.*, **56**, 1837, 1923,

Thorite. Lead from Norwegian Thorite supplied by Fajans. **Part** of sample used by Honigschmid to determine atomic weight 207.90.¹

Wilberforce. Origin pitchblende from Wilberforce, Ontario. Methyl prepared from chloride used by Baxter to get atomic weight 206.195.²

Bear Lake. Uranium lead from Great Bear Lake, Canada. Reported to have an atomic weight about 205.95.

Morogoro. Lead from pitchblende from Morogoro, East Africa.

TABLE OF RESULTS

Lead.	206.	207.	208.	Mean Mass Number.
Katanga I and II	93.3	6.7	(0.02)	206.067
Thorite. . . .	4.6	1.3	94.1	207.895
Wilberforce	85.9	8.3	5.8	206.199
Bear Lake	89.8	7.9	2.3	206.102
Morogoro .	931	6.9	0	206.069

The results obtained from lead extracted from Swedish Kolm³ were unsatisfactory but indicated no particular difference from other uranium leads. Some of these results have been discussed in connection with the Actinium problem.⁴

The Titanium Group.

These elements do not form stable methyls and their volatile compounds are not suitable for use in the discharge. As a consequence mass-spectra have only been obtained from the lighter members of the group with the greatest difficulty by the methods of anode rays.

22. *Titanium.*

The first attempts on this metal were made with its volatile chloride but failed, for, owing to the violent action of this compound on parts of the apparatus, the mass-spectra were too complex for identification.⁵ In a later experiment with accelerated anode rays⁶ potassium titanifluoride was first used in the anode. On the mass-spectra produced faint indications of a line at 48 could be seen, but were valueless for the following reason: A fairly strong line appeared at 47. This was undoubtedly due to Si²⁸F so that part, if not all, the effect at 48 could be ascribed to Si²⁹F. A later experiment, in

¹ Fajans, *Zeit. Electrochem.*, 25, 91, 1919.

² Baxter and Bliss, *Jour. Amer. Chem. Soc.*, 52, 4951, 1930.

⁸ *Ibid.*, p. 4848.

⁴ Grosse, *Phys. Rev.*, 42, 565, 1932.

⁵ Aston, *Phil. Mag.*, 45, 937, 1923.

⁶ *Ibid.*, 47, 397, 1924.

which the fluoride made by the action of hydrofluoric acid on the pure oxide was used, proved more successful. This gave a line at 48 not only reasonably strong but much stronger than that at 47 now feeble, from which it may be safely concluded that the principal, if not the only, isotope of titanium is of mass number 48. It will be a matter of great difficulty to prove or disprove the existence of other less abundant mass numbers, though one lighter one at least is suggested by the chemical atomic weight 47.90.

40. Zirconium.

Many abortive attempts were made to obtain the lines of this element and success with the first mass-spectrograph was only obtained by the fortunate combination of an exceptionally good setting of the anode-ray discharge tube and a remarkably sensitive schumannized plate.¹ The anode contained a mixture of zirconium fluoride and lithium fluoride, but a considerable quantity of bromine was present from previous experiments. Three of the lines 90, 92, 94, can be ascribed with confidence to zirconium. A fourth faint one (96) is doubtful, but may be another isotope. A very rough estimate of their relative abundance is 10, 2, 4, (1), respectively. The masses were found integral with bromine to the accuracy of experiment. No data on zirconium have been obtained since, but if we assume its packing fraction to be the same as that of bromine, and omit the doubtful isotope 96, the estimate of abundance is in good agreement with the latest value of the chemical atomic weight 91.22.

72. Hafnium.

There is good reason to expect that the mass rays of this element should be obtainable by the same means as those used for zirconium, though their greater mass would make them harder to detect. Many experiments have been tried with a variety of hafnium compounds, but so far without the least success.

90. Thorium.

From the experience with zirconium and hafnium it is probable that effects will only be obtained from thorium with extreme difficulty. This is unfortunate, as direct evidence on the isotopic constitution of this element would be of great value in connection with the theories of radioactivity.

¹ Aston, *Phil Mag.*, 49, 1195, 1925.

GROUP V

7. *Nitrogen.*

Owing to its presence in the air this element was one of the first recorded by positive ray analysis. Its examination by the first mass-spectrograph was difficult, as its atom could not be distinguished from CH_2 nor its molecule from CO . Its second-order line appeared to correspond to a mass exactly 7,¹ and it was assumed to be a simple element, as was to be expected from its chemical atomic weight 14.008.

The determination of its packing fraction by means of the second mass-spectrograph² was unsatisfactory owing to the impossibility of disentangling its lines from those of carbon compounds, while at the same time making use of the latter for reference ratios. By the use of mixtures of nitrogen and ethane in varying proportions some success was obtained, and the results indicated the most probable value of its packing fraction to be 6.0 giving a mass 14.008.

The discovery of the isotopic nature of oxygen and the resulting shift of the mass scale led to a search for heavier isotopes of nitrogen and the second rare component 15 was discovered by Naude³ in the band spectra of NO . In his later report⁴ he estimates the ratio of abundance of N^{14} to N^{15} to be 700 ± 140 . Naude's work was supported by that of Herzberg⁵ who estimated the ratio at 800. Herzberg also searched for an isotope 16, theoretically predicted, but this was not found. Later estimates of the ratio of abundance are considerably lower. Birge and Menzel⁶ taking Mecke's values for the oxygen isotopes, calculate that it should be 320 in order to bring the writer's figure for the mass of N^{14} into agreement with the chemical atomic weight. Urey and Murphy⁷ from their measurement of absorption bands give for the ratio of abundance of $\text{N}^{15}\text{O}^{16}$ to $\text{N}^{14}\text{O}^{18}$ the preliminary value 0.551 ± 0.062 . Assuming Mecke's value for the ratio O^{16} to O^{18} this gives for the nitrogen ratio 347.

From optical spectrum data Birge⁸ obtains two values 14.999 and 15.0065 for the mass of N^{15} and takes a mean value corresponding to an isotopic weight 15.0027 and a packing fraction 2.0. In consideration of the uncertainties both in the abundance of N^{15} and in the isotopic weight of N^{14} the physical results are in good agreement with the chemical atomic weight 14.008.

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

² Aston, *Proc. Roy. Soc. A*, **115**, 503, 1927.

³ Naude, *Phys. Rev.*, **34**, 1498, 1929. ⁴ *Ibid.*, **36**, 333, 1930.

⁵ Herzberg, *Z. f. Phys. Chem.*, Bd. 9, 43, 1930.

⁶ Birge and Menzel, *Phys. Rev.*, **37**, 1669, 1931.

⁷ Urey and Murphy, *Phys. Rev.*, **38**, 575, 1931,

⁸ Birge, *Phys. Rev.*, **37**, 841, 1931.

IS. *Phosphorus.*

This element can be conveniently examined by means of its gaseous hydride PH_3 which gives four lines 31, 32, 33, 34. As these clearly corresponded to P, PH, PH_2 , PH_3 and no others could be seen, it was assumed that phosphorus was a simple element.¹

In order to determine its packing fraction advantage was taken of the fact that the numerical ratio CO : P is sufficiently close to P : PH_3 to give the small intervals necessary for the application of method III.² If the pair CO, P is photographed between the slightly wider pair P, PH_3 as indicated in Spectrum VIII, Plate VI, the two intervals can both be measured on the same spectrum, though it was found safer to bring them into the same position on the plate by a second exposure.³ The packing fraction found in this way was — 5.6 corresponding to a mass of 32.9825. Making the customary correction to the chemical scale we get 30.978. This is so much lower than the value 31.02 obtained by purely chemical methods that heavier isotopes have been suggested.⁴ On the other hand, Ritchie's recent determination of the density of phosphine⁵ gives a value 30.977 in striking agreement with that obtained with the mass-spectrograph.

33. *Arsenic.*

This element was examined at the same time as phosphorus by means of its gaseous hydride AsH_3 . The spectrum obtained, shown in Spectrum IX, Plate IV, was similar to that obtained with phosphorus, so it was concluded to be a simple element of mass number 75. The packing fraction of arsenic was determined by the comparison of its hydrides with bromine by the method of series shift,⁶ using a shift of one unit. The interval $\text{AsH}_3, \text{Br}^{79}$ was measured against As, AsH on the one side and $\text{Br}^{79}, \text{Br}^{79}\text{H}$ on the other. The difference between the packing fractions is very small, 0.2, so if we take that of Br^{79} as — 90, that of arsenic is — 8.8 and its mass 74.934. This reduced to the chemical scale becomes 74.92 in good agreement with the present value 74.93.

51. *Antimony.*

The first experiments on this element made with the hydride SbH_3 gave negative results which were ascribed to the unstable nature of the compound.⁷ Later the vapour of the methyl was used mixed with

¹ Aston, *Phil. Mag.*, 40, 632, 1920.² V. p. 81.³ Aston, *Proc. Roy. Soc. A*, 115, 504, 1927.⁴ Naudé, *Phys. Rev.*, 36, 346, 1930.⁵ Ritchie, *Proc. Roy. Soc. A*, 128, 578, 1930.⁶ V. p. 80.⁷ Aston, *Phil. Mag.*, 42, 141, 1921.

CO₂ with success.¹ Its spectrum is characterized by two strong lines 121, 123. Similar pairs appear 15 and 30 units higher in the mass scale due to the mono- and di-methyl molecules respectively. Faint companions at 122 and 124 are safely to be ascribed to hydrides.

By photometry of the antimony lines on spectra obtained later with the second mass-spectrograph² the ratio of the abundance of the isotopes 121 and 123 was estimated to be 100 : 78.5 giving a mean mass number of 121.88 and an isotopic moment of 0.96. The packing fraction of antimony has not yet been measured but if a value intermediate between that of tin and that of xenon is assumed the atomic weight on the chemical scale works out to be 121.79 in good agreement with the international value 121.76.

83. *Bismuth.*

The only data so far available for bismuth were obtained by accelerated anode rays.³ Metallic bismuth was ground into the anode paste and after a long exposure with the anode worked at a white heat it gave a single line at the position expected from its atomic weight 209.00. This line was faint and its position not measurable with any great accuracy, but there is no reason to doubt that bismuth is substantially simple of mass number 209.

The Vanadium Group.

23. *Vanadium.*

This element was investigated during the first set of experiments with accelerated anode rays.⁴ An anode consisting of vanadium chloride mixed with lithium iodide was used. A single line appeared in the expected position corresponding to mass number 51. This was compared with K³⁹ on the one side and with Fe⁵⁶ on the other and appeared integral with them to the accuracy of measurement. No further data are available. The chemical atomic weight 50.95 is virtually in exact agreement with a packing fraction fitting the curve so that there is unusually strong evidence that vanadium is a simple element.

41. *Niobium.*

All the early attempts to analyse this element by the same means which had succeeded in the case of vanadium gave negative results. It was only quite recently that success has been achieved by the use

¹ Aston, *Phil. Mag.*, **45**, 943, 1923.

² Aston, *Proc. Roy. Soc. A*, **132**, 492, 1931.

³ Aston, *Phil. Mag.*, **49**, 1197, 1925.

⁴ *Ibid.*, **47**, 397, 1924.

of its volatile pentafluoride.¹ Its mass-spectrum shows only one line 93 with fluorides at 102, 121 It has not been possible to measure the packing fraction of niobium with accuracy but comparison with line 85 (SiF_6) suggests a large negative value about -8 . This indicates an atomic weight on the chemical scale of 92.90 ± 0.05 , a value much lower than the International figure at present in use.

73. *Tantalum.*

This element resisted all attempts until it was analysed by means of its pentafluoride at the same time as niobium. Like the latter, it proved to be simple, giving a single line at 181 followed by 200, 219 due to TaF , TaF_2 Neither the line at 183, expected from its atomic weight, nor any other could be detected even to one-fiftieth the intensity of the main line. Its packing fraction was estimated to be -4 from the position of line 200 in the mercury group. This gives an atomic weight 180.89 ± 0.07 on the chemical scale suggesting that the higher chemical value 181.4 needs revision.

91. *Protactinium.*

Of the possible radioactive isotopes of atomic number 91 one only, protactinium, the parent of the actinium series, has a sufficiently long average life to hold out any hope of accumulation in chemical quantity.² This is now being done and in course of time it is hoped to determine its atomic weight which is expected to correspond to mass number 231.

¹ Aston, *Nature*, **130**, 130, 1932.

² v. Grosse, *Jour. Am. Chem. Soc.*, 52, 1742, 1930.

CHAPTER XII

GROUPS VI, VII AND VIII

GROUP VI

8. Oxygen.

This element, the most abundant in Nature and the primary standard of chemical atomic weights, is present, in chemical combination, in all ordinary forms of discharge tube and so may be expected to appear to a greater or less extent on all mass-spectra obtained by their means. During the early work on positive ray analysis its molecular line at 32 and its atomic lines of the first and second order at 16 and 8 were, very naturally, chosen as convenient standards of mass. When by means of the second mass-spectrograph accuracies of the order of 1 in 10,000 were attained and the deviations from the whole-number rule measured, oxygen was defined to have a zero packing fraction and its neutral atom O^{16} definitely adopted as the standard of atomic mass on the physical scale. The results then obtained^x appeared in good accordance with the generally accepted idea that oxygen was essentially a simple element and that therefore the chemical and physical scales were virtually identical; the disintegration photographs of Blackett² suggested that O^{17} was at least capable of existence, but no evidence of its presence in appreciable quantity had been observed.

Much interest was raised in 1929 by the announcement by Giauque and Johnston³ of an isotope of mass 18. Direct measurements with the mass-spectrograph showed that it could not be present to an extent greater than 1 in 500⁴ and a later communication from the discoverers⁵ gave an estimate of abundance well below that estimate and also announced a further discovery of a still rarer isotope 17. These discoveries were made by the analysis of the spectra of the atmospheric absorption bands photographed by Dieke and Babcock,⁶ which when interpreted on the quantum theory afforded unambiguous proof of the existence of molecules $O^{16}O^{18}$ and $O^{16}O^{17}$ in the atmosphere.

¹ Aston, *Proc. Roy. Soc. A*, **115**, 487, 1927.

² Blackett, *Proc. Roy. Soc., A*, **107**, 349, 1925.

³ Giauque and Johnston, *Nature*, **123**, 318, 1929.

⁴ Aston, *Nature*, **123**, 488, 1929.

⁵ Giauque and Johnston, *Nature*, **123**, 831, 1929.

⁶ Dieke and Babcock, *Proc. Nat. Acad. Sci.*, **13**, 670, 1927.

The determination of the relative abundance is a matter of some difficulty. The first estimate of the ratio O^{16} to O^{18} was given by Babcock * as 1250 with a probable error of 25 per cent. Naude,² working with the absorption bands of NO, which present certain advantages over those of oxygen, gave a value 1075 ± 10 . More recently from an exhaustive examination of the atmospheric absorption bands Mecke and Childs³ give as their best mean 630. They give for the ratio of O^{18} to O^{17} a value 5 as against 8 estimated by Babcock and Naude.

Smythe and Mattauch⁴ investigated the intensity of the peaks of lines 32 and 34 given by a discharge in oxygen by means of their mass-spectrometer and concluded that the ratio of O^{16} to O^{18} is greater than 600. The intensities of the molecular lines of oxygen have been compared directly by the second mass-spectrograph, their brightness being enhanced by the presence of helium in the discharge.⁵ Line 32 was found to be 268 times as intense as line 34, which was 4.2 times as intense as line 33. These figures correspond to ratios of abundance 536 and 4.2 but can only be regarded as rough minima, for owing to the action of the oxygen discharge on the wax and grease it is certain that sulphur is present, and if to the extent of 1 per cent, would enhance line 34 by about 10 per cent, and line 33 even more. It appears very desirable that direct measurements on mass-spectra should be made under conditions precluding the presence of sulphur, for this seems the most reliable method of arriving at the value of the ratio between the physical and chemical scales. The International Atomic Weights Commission have adopted a factor 1.00022 founded on Mecke and Child's ratios of abundance, but a general survey of the relations between the measurements of the masses of the isotopes and the chemical atomic weights of the elements suggests that this factor is too high.

The masses of O^{17} and O^{18} are exceptional in that they can be compared with the standard O^{16} by purely optical methods. In this way they have been computed by Birge⁶ to be 170029 and 180065 respectively.

16. Sulphur.

This element was first investigated by means of its compound sulphur dioxide.⁷ Results then obtained are shown in Plate IV, Spectra VII and VIII. Above each is a comparison spectrum taken

¹ Babcock, *Proc. Nat. Acad. Sci.*, 15, 471, 1929; *Phys. Rev.*, 34, 540, 1929.

² Naudé, *Phys. Rev.*, 36, 333, 1930.

³ Mecke and Childs, *Zeits. f. Physik.*, 68, 362, 1931.

⁴ Smythe and Mattauch, *Phys. Rev.*, 40, 429, 1932.

⁵ Aston, *Nature*, 130, 22, 1932. ^e Birge, *Phys. Rev.*, 37, 841, 1931.

⁷ Aston, *Phil. Mag.*, 40, 631, 1920.

immediately before the gas was admitted, on the same plate and with approximately the same fields. The lines 32, 33, 34 were clearly due to the introduction of sulphur. Line 32 was certainly due to the element itself, but experience had shown that the oxygen line 16 was almost invariably accompanied by lines 17 and 18 which were certainly due to OH and OH₂, hence similar hydrides SH and SH₂ were to be expected. The chemical atomic weight 32.06 certainly suggested isotopes of higher mass number, but the apparatus was quite incapable of separating the line due to O₂ from that of a sulphur of mass 32.06 if that existed. Hence it seemed safest to rest content with the certain conclusion that atoms of mass number 32 were present in preponderating proportion. As soon as the second mass-spectrograph was found to be capable of resolving doublets such as oxygen, methane, the matter was put to a direct test.¹ Spectra were obtained under conditions such that both O₂ and S must have been present, but the line 32 showed no signs of doubling. This proved that the atom of S³² could not have a mass 32.06 so that atoms of higher mass number must be present. Further tests showed that the faint companions 33, 34 (S); 49, 50 (SO) ; 65, 66 (SO₂), etc., were present on all spectra, even when the conditions were such as to make the presence of hydrides very unlikely. The intensity relations of the lines were also strongly indicative of true isotopic character. As a final confirmation a negative mass-spectrum of SO₂ was taken by exposing for an hour with both fields reversed. Lines 32, 33, and 34 were all visible and again showed the same intensity relations. We may safely conclude that sulphur, like magnesium and silicon, the two elements of even atomic number which precede it, is a triple element. The lightest mass number is by far the most abundant in all these three complex elements. S³⁴ appears to be about three times as abundant as S³³, the two together amounting to about 3 per cent, of the whole. The three lines of sulphur can be seen in Spectrum VII, Plate IV. No measurements of the packing fractions of the atoms of sulphur have yet been made.

34. *Selenium.*

Early attempts to analyse this element by means of its gaseous hydride were completely unsuccessful,² but by vaporizing the element itself in the discharge tube conclusive results were at once obtained.³ The mass-spectrum was characterized by five strong lines 76, 77, 78, 80, 82 and a faint sixth 74. The true isotopic nature of this group was beautifully brought out by its repetition at a position 12 units

¹ Aston, *Proc. Roy. Soc. A*, 115, 487, 1927.

² Aston, *Phil. Mag.*, 42, 140, 1921.

³ *Ibid.*, 45, 941, 1923.

higher on the mass scale due to CSe and 28 units higher due to COSe. The evidence of the isotopic constitution of selenium was therefore exceptionally definite and trustworthy. The relative abundance of the selenium isotopes was later determined by the photometry of its lines obtained by means of the second mass-spectrograph,¹ using the vapour as before. The following figures were obtained :

Mass number .	. 74	76	77	78	80	82
Abundance .	. 0.9	9.5	8.3	240	480	9.3

The value for 76 is suspect, as almost all mass-spectra taken in this region with an ordinary discharge show traces of a line at this point. Its origin is unknown and may be CS₂. Other possibilities are CO₂S, Si²⁸OS or Si²⁸O₃. There is, however, no doubt that the intensity from this unknown source cannot be more than a very small fraction of the total intensity of line 76 when plenty of selenium vapour is present.

These figures give an isotopic moment of 1.49 and a mean mass number of 79.023. There was not the slightest indication of 79 or 81 recently predicted by Johnson,² these mass numbers could have been detected if present to 0.2 per cent.

In order to measure the packing fraction of selenium methyl bromide was introduced into the discharge. It is of interest to record that this increased the brightness of the selenium lines to a very marked degree, probably by the action of the bromine ions on the selenium on the walls. The series of lines 78, 79, 80, 81 were now examined by the method II "series shift"³ using a shift of slightly less than one unit of atomic weight checked by another of slightly more than one unit. The HBr lines were much too faint to cause any appreciable error in these measurements. The small intervals were estimated by means of the photometer, and although the slits fitted in the mass-spectrograph at the time were not fine enough for really accurate work, consistent results were obtained indicating that both Se⁷⁸ and Se⁸⁰ have negative packing fractions less than Br⁷⁹ and Br⁸¹. The best mean value for Se⁸⁰ is — 7.3 with an extreme uncertainty of ± 2 . That of Se⁷⁸ appears to be nearer — 80, but could not be determined so accurately. Correcting the mean mass number given above for packing fraction and change of scale the atomic weight works out at 78.96 ± 0.04 , a value considerably lower than the chemical value now in use (79.2), but which has been exactly confirmed by the latest determination by Honigschmid⁴ who, by employing the most accurate modern methods, has obtained the value 78.962 ± 0.002 .

¹ Aston, *Proc. Roy. Soc.*, **132**, 487, 1931.

² Johnson, *Jour. Amer. Chem. Soc.*, **54**, 824, 1932.

³ V. p. 80.

⁴ Honigschmid, *Naturwiss.*, **35**, 659, 1932.

52. *Tellurium.*

This element is of peculiar interest on account of the anomalous position of its atomic weight with regard to that of iodine in the periodic table. Its properties are not by any means suitable for the production of mass rays and it was in fact the last of the non-metallic elements to be analysed. The early trials with tellurium methyl,¹ and then by volatilizing tellurium or its chloride² all failed, but success was achieved to a certain degree by the method of accelerated anode rays when pure tellurium was introduced into the anode.³ The effects were not strong, but sufficient to identify three isotopes 126, 128, 130. Rough estimates of abundance suggested an atomic weight at least 128.

Later experiments with tellurium chloride, made with the second mass-spectrograph, though giving feeble results, enabled a new faint isotope 125 to be revealed and the relative abundances to be directly determined by photometry.⁴ Line 125 was estimated at 6.6 and 126, 128, 129 at 20.9, 36.1, and 36.4 per cent, respectively. It was also found possible to measure the packing fraction of the lines 126 and 128 by comparing them with I^{127} , this may be taken as -5 ± 2 .

These values were not in good agreement with the accepted chemical atomic weight 127.5, but a little later this discrepancy was removed by the work of Bainbridge,⁵ who by volatilizing tellurium was able to produce excellent mass-spectra such as that shown in Plate VII. These disclosed three additional isotopes 124, 123, 122 and indications of an extremely faint and doubtful one 127. Using the writer's figures, given above, for the stronger lines, to calibrate his plate, Bainbridge works out the following values:

Mass number	.	122	123	124	125	126	127	128	130
Abundance	.	2.9	1.6	4.5	60	190	?	32.8	33.1

giving an isotopic moment 1.74 and mean mass number 127.67. By correcting for packing fraction and change of scale the atomic weight of 127.58 ± 0.15 is obtained in exact agreement with Honigschmid's⁶ latest chemical value 127.587 ± 0.018 .

84. *Polonium.*

A search for an inactive isotope of this element has been made by Hevesy and Guenther⁷ who examined a large number of probable minerals by a special method of extraction employing polonium itself as a radioactive indicator to control the process. The final extracts

¹ Aston, *Phil. Mag.*, 42, 241, 1921.

² *Ibid.*, 45, 942, 1923.

³ *Ibid.*, 49, 1197, 1925.

⁴ Aston, *Proc. Roy. Soc. A*, 132, 487, 1931.

⁵ Bainbridge, *Phys. Rev.*, 39, 1021, 1932.

⁶ Honigschmid, *Naturwiss.*, 35, 659, 1932.

⁷ Hevesy and Guenther, *Nature*, 125, 744, 1930.

were subjected to X-ray analysis, but no inactive element was found although 10^{-n} grm. per gramme of mineral was detectable.

The Chromium Group.

The early work on this group of metals was by no means promising. One faint line only was obtained from chromium itself and in the survey given in 1925¹ its heavier homologues were classed among the least hopeful elements for analysis. Recently, however, the situation has been reversed and the preparation of the volatile carbonyls has enabled a very complete analysis to be made with most interesting results.

24. *Chromium.*

The first successful experiment with this element was made by the use of an anode containing halides of chromium.² One line only appeared at 52 and as this agreed exactly with the chemical atomic weight chromium was regarded as a simple element. The application³ of the more powerful and convenient method of the ordinary discharge tube has now been made possible through the preparation of a suitable volatile compound, the hexacarbonyl. The vapour pressure of this white crystalline solid is appreciable at ordinary temperature but not high enough to give a sufficient flow through the customary fine glass "leak." The latter was therefore not used, but instead the vapour was allowed to diffuse directly into the discharge bulb with no more obstruction than two stopcocks and a few centimetres of narrow bore tubing. Even with this arrangement the rate of diffusion was so low that no difficulty was experienced in keeping the pressure down by slow pumping.

The beams of rays obtained were vastly more intense than those given by the anode rays and it was soon realized that chromium had four isotopes, 50, 52, 53, 54, of which 52 was much the strongest. Of these the lightest is isobaric with the doubtful Ti⁵⁰ and the heaviest with Fe⁵⁴. It was impossible to hold the discharge constant for any considerable length of time and the relative abundance was determined by the method of intermittent exposures, with the following results:

Mass number	.	.	.	50	52	53	54
Abundance	.	.	.	.4 .9	81.6	10.4	3.1

The concentration of the weight in one isotope gives chromium the very low isotopic moment 0.31 and at the same time enables the mean mass number to be fixed with unusual accuracy at 52.068.

A provisional value for the packing fraction of chromium was

¹ Aston, *Phil. Mag.*, **49**, 1200, 1925.

² *Ibid.*, **47**, 397, 1924.

³ Aston, *Proc. Roy. Soc. A*, **130**, 306, 1931.

obtained by comparing its 52 line with $\text{C}_0 8$ 44. The only near ratio available for this was $\text{C}:\text{CH}_2$. The latter line was introduced by allowing a trace of methane to flow into the discharge tube with the vapour of the carbonyl, but its exact mass is doubtful owing to the presence of Si^{28++} and possibly C_0^{++} and N . In addition the two ratios have too large a numerical difference for really accurate measurement. From the data obtained the most probable value of the packing fraction appears to be — XO. Correcting for this and change of scale the atomic weight is 52.006, a value virtually identical with 52.01 the one accepted from chemical determinations.

42. *Molybdenum.*

The first attempts to obtain the mass-spectrum of the element were made by the method of accelerated anode rays. These were entirely unsuccessful * and the chance of obtaining a suitable volatile compound seemed remote until a specimen of the carbonyl, probably $\text{Mo}(\text{CO})_6$, was prepared. This is very like the chromium compound in volatility and other physical properties and was found to work almost as satisfactorily when admitted to the discharge bulb in exactly the same way.²

The chemical atomic weight of molybdenum is practically a whole number, and Russell, by a theory markedly successful in many cases and founded on analogies from the known radioactive disintegrations, had confidently predicted it to be a simple element of mass number 96.³ It was therefore somewhat surprising to find that its mass-spectrum contained no less than seven lines, 92, 94, 95, 96, 97, 98, 100, three of which form isobaric pairs with Zr^{92} , Zr^{94} and the doubtful Zr^{96} . This group shows a similarity of abundance more striking than that of any other element of such complexity.

The total intensity of the group of molybdenum rays was probably less than that yielded by chromium and as this is divided among seven almost equal fines it was by no means easy to get lines dark enough for good photometry even with the maximum practicable exposures. For this reason the group had to be photographed at a position on the plate giving less than the normal resolution. Under these conditions it was only just possible to use the method of intermittent exposures. The small range of intensity rendered a single ratio of 2 to 1 sufficient for the measurements, but the extreme closeness of the lines impairs the accuracy of the photometry so that the ratio must be taken as less certain than usual.

A further difficulty was the inevitable presence of the doubly charged mercury group. The very weak line Hg^{196++} could be virtu-

¹ Aston, *Phil. Mag.*, 47, 399, 1924. ² Aston, *Proc. Roy. Soc. A*, 130, 308, 1931.

³ Russell, *Nature*, 112, 588, 1923.

ally eliminated, but even with the utmost precautions it was not possible to reduce Hg^{200++} below a considerable fraction of the practically coincident line Mo^{100} . In order to arrive at the true line intensity of the latter the lines of the mercury group had to be photometered up and the effect of the mercury line, estimated from the known ratios of intensity of the mercury group, subtracted. Incidentally these measurements showed that no molybdenum lines of appreciable strength could be present at 99 or 101. On account of these difficulties no great accuracy can be claimed for the abundance ratios then obtained which are as follows :

Mass number	. 92	94	95	96	97	98	100
Abundance	. 14.2	100	15.5	17.8	9.6	23.1	9.8

These results which must be taken as provisional only, give for molybdenum an isotopic moment of 1.87, the highest yet measured, and a mean mass number 96.025.

A provisional value for the packing fractions of Mo^{98} and Mo^{100} was obtained by estimating the position of these lines among those of mercury. It is — 5.5, only a rough value but adequate for calculating the atomic weight. It is a definitely smaller negative value than that expected from the packing fraction curve. The atomic weight of molybdenum on the chemical scale works out to be 95.95 ± 0.06 in reasonable agreement with 96.0 now in use.

74. *Tungsten.*

An attempt to obtain the mass-spectrum of this element by means of its volatile hexafluoride was unsuccessful,¹ but good results were obtained later with the second mass-spectrograph by the use of its hexacarbonyl.² The procedure adopted was the same as that with the corresponding compound of molybdenum, but owing to its smaller volatility and the greater atomic weight of tungsten the effects were much weaker and it was only by long exposures and the use of Q plates that lines of satisfactory intensity were obtained. Tungsten has four isotopes of which the two strongest give lines of practically identical intensity. In order to measure the relative abundance of its constituents it was assumed that their photographic effect would be the same as that of the slightly heavier ones of mercury. The lines of the latter were, therefore, photographed on the same plate with a graduated series of suitably short exposures. From the known abundance of the mercury isotopes those of tungsten were deduced with the following results:

Mass number	. . .	182	183	184	186
Abundance	. . .	22.6	17.3	30.2	29.9

¹ Aston, *Proc. Roy. Soc. A*, 115, 507, 1927. ² *Ibid.*, A, 132, 491, 1931.

The packing fraction of tungsten has not been measured with accuracy, but owing to the nearness of the mercury lines on the mass scale it was possible by measurements of their relative positions to prove that they were related as whole numbers to within 1 part in 2000. Adopting therefore a value zero for the packing fraction and correcting to the chemical scale the atomic weight is 183.93 in agreement with the accepted chemical value of 184.0.

92. *Uranium.*

Determinations of the constitution of this, the heaviest known element, are of the utmost importance in connection with the subject of radioactivity. Unfortunately its properties are not at all favourable to the production of mass rays, and it is only quite recently that its mass-spectrum has been obtained by means of its volatile hexafluoride.¹ It appears simple to at least 97 per cent. Its line, mass number 238, was photographed of satisfactory strength followed by series of fluoride molecules 257 UF, 276 UF₂ The last line visible in this series, 333, corresponded to UF₅ is the heaviest mass definitely recorded on a mass-spectrum. Owing to technical difficulties connected with the polarization of the electric plates it was not possible to determine its packing fraction, but it appears very improbable for it to have a positive value high enough to agree with the chemical atomic weight 238.14 at present accepted.

GROUP VII

The Halogens.

These elements are particularly favourable to mass-ray analysis. They not only provide many suitable volatile compounds for use in the ordinary discharge but are essential for the production of anode rays. In consequence our knowledge of their isotopic constitution is unusually complete and their lines provide valuable standards of mass.

9. *Fluorine.*

So far the most convenient source of fluorine rays is the gas boron fluoride. When this compound was first examined² a strong line at 19 with a second-order line at 9.5 led to the conclusion that these were due to fluorine which, on account of its chemical atomic weight, was assumed to be simple. The line 20 which appeared in some spectra was clearly due to HF. Spectra given by BF₃ are reproduced in Plate IV.

The packing fraction of fluorine was measured on the second mass-

¹ Aston, *Nature*, 128, 725, 1931.

² Aston, *Phil. Mag.*, 40, 629, 1920.

spectrograph¹ by means of the approximate ratio C:CH₈, F:C₂. Spectra I I I and IV, Plate V, are examples of the results ; the measurements gave negligibly small packing fractions as often negative as positive, with a mean practically zero. On account of the difference between the scale this suggests an atomic weight rather less than 19*00, the value in chemistry, but the difference only affects the third decimal place and is too near possible experimental error to warrant the conclusion of heavier isotopes. They are, however, suggested by Cawood and Patterson² who from the density of methyl fluoride obtain the high value 19.011 for the atomic weight.

17. Chlorine.

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 (COCl₂) was substituted.³ Spectra I I, I I I, and IV, Plate I I I, 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 that chlorine is characterized by the appearance of four very definite lines in the previously unoccupied space to the right of O₂ (32) : measurement shows these lines to correspond exactly to masses 35, 36, 37, and 38. On Spectrum I I, Plate I I I, 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 Cl³⁵ and Cl³⁷ are the main if not the only constituents is given by the strong lines 63 and 65 (Spectrum IV, Plate I I I), due to COCl³⁵ and COCl³⁷. The lines 36 and 38 were naturally ascribed to the hydrochloric acids corresponding to Cl³⁵ and Cl³⁷. 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. 54. 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

¹ Aston, *Proc. Roy. Soc. A*, 115, 487, 1927.

² Cawood and Patterson, *Jour. Chem. Soc.*, 2180, 1932.

³ Aston, *Phil. Mag.*, 39, 620, 1920.

faint line is distinguishable at 39. This was regarded as a possible third isotope which would then be an isobare of potassium. Further evidence rendered this conclusion unlikely. During some experiments with tellurium chloride,¹ exceedingly dense lines were obtained at 35, 36, 37, 38, with no vestige of a line at 39. This makes it certain that the hypothetical isotope 39 does not exist in any appreciable quantity.

The evidence obtained from optical spectra on the possibility of an isotope 39 is conflicting. Observations on the infra-red spectrum of HCl led Becker² to conclude that it was present and a further investigation of the same phenomena by Hettner and Bohme³ gave the same results. On the other hand, Ashley and Jenkins⁴ from the analysis of the ultra-violet absorption bands of AgCl calculate that Cl³⁹ cannot be present to a greater extent than 1 in 4400 of Cl³⁵. The absence of Cl³⁹ has also been confirmed in the infra-red absorption spectra of HCl by Hardy and Sutherland.⁵

The packing fractions of the isotopes of chlorine are known with considerable certainty, that of Cl³⁵ was measured in three different ways. First by the use of a mixture of COCl₂ and CO₂ the approximate series CO : Cl³⁵ : CO₂ was tested. Then by the addition of argon which had already been measured, the ratio Cl³⁵ : CO was compared with A⁺⁺ : 0. Finally Cl³⁵ was compared directly with PH₃ by Method II. The results of all were consistent and gave the most probable packing fraction as — 4.8 giving a mass 34.983. Cl³⁷ was compared with CO by the approximate ratio C : 0, and also CH₃ : A⁺⁺, finally checked by comparison with Cl³⁵ by Method II. These gave for Cl³⁷ a value - 5.2 and mass 36.980.⁶

Direct measurements of the abundances of the chlorine isotopes are by no means satisfactory. The ratio is too high for really accurate photometry and a further uncertainty is caused by the wide spacing of the lines and probable difference in photographic efficiency. The actual values obtained⁷ ranged from 30 to 31 whereas calculations from the chemical atomic weight gives 3.18.

35. Bromine.

The early results with this element were definite and easy to interpret.⁸ Its chemical combining weight is known with great cer-

¹ Aston, *Phil Mag.*, 45, 943, 1923.

² Becker, *Zeit. f. Physik.*, 59, 583 ; 601, 1930.

³ Hettner and Bohme, *Zeit. f. Physik.*, 72, 95, 1931.

⁴ Ashley and Jenkins, *Phys. Bev.*, 37, 1712, 1931.

⁵ Hardy and Sutherland, *Phys. Rev.*, 41, 471, 1932.

⁶ Aston, *Proc. Roy. Soc. A*, 115, 487, 1927.

⁷ *find.*, A, 132, 497, 1931.

⁸ Aston, *Phil Mag.*, 40, 631, 1920.

tainty, 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.

The packing fractions of the two isotopes of bromine were determined by means of the second mass-spectrograph¹ using methyl bromide as before. Some of the spectra obtained are reproduced in Plate V. It is of interest to note that the third-order line of Br⁷⁹ was obtained for the first time; it can be seen clearly at 26.3 on Spectrum VI, that of Br⁸¹ being masked by C₂H₃. The second-order line of Br⁸¹ at 40.5 was compared with C₂O₂ by means of the ratio C : CH giving as the mean probable value of its packing fraction — 8.6 and mass 80.926. Br⁷⁹ was then compared with Br⁸¹ by a series shift of one unit as described under Method II.² The mean difference shown was 0.4 giving — 9.0 as the packing fraction of Br⁷⁹ corresponding to mass 78.929.

Throughout the earlier work on mass-spectra no certain difference of intensity could be observed between the two lines of bromine 79 and 81. Accurate photometry has now supported that conclusion.³ Many plates showing the bromine lines have been examined photometrically from time to time, and though on the average the 79 line was more intense than that at 81 the difference was just about cancelled by the correction for position. The plates obtained with methylene bromide and selenium contained many spectra suitable for this test, and the best mean value of the difference was cancelled well within the probable error by the correction for position. It can, therefore, be assumed that the ratio of relative abundance of its two isotopes, and in consequence its isotopic moment, differs from unity by an insignificant amount.

If we assume exact equality and correct the mean weight to the chemical scale the atomic weight works out to be 79.911, a value in good agreement with the International one 79.916.

¹ Aston, *Proc. Roy. Soc. A*, **115**, 487, 1927.

² *V.* p. 80.

³ Aston, *Proc. Roy. Soc. A*, **132**, 489, 1931.

53. *Iodine.*

The early results with this element¹ were both definite and conclusive. Methyl iodide was used, its vapour being mixed with CO_2 and CH_4 . It gave one strong line at 127 satisfactorily confirmed by another at 142 due to CH_3I . It was concluded that iodine was a simple element and so far there is no evidence against this. The line of iodine is always very easy to produce and in experiments on anode rays it was noticed that it always gave a strong line, although those of the other halogens were seldom perceptible, even though they were present in the anode in much greater proportion.²

The determination of the packing fraction was made by the direct comparison of the single line with Xe^{128} .³ No difference between the packing fractions could be observed so that that of iodine can be taken as the same as that of xenon, namely — 5.1. This gives a mass on the physical scale of 126.932 which after change of scale is in excellent agreement with the latest International chemical atomic weight 126.92.

84. (*Ekaiodine*).

The existence of an element of this atomic number has not yet been proved. A critical search for it in pitchblende made recently by Hevesy and Hobbie⁴ gave a negative result although 1 part in 10^9 could have been detected.

The Manganese Group.

25. *Manganese.*

The only results recorded for manganese are those obtained with the first mass-spectrograph by the method of accelerated anode rays. Manganese fluoride and lithium iodide were used in the anode mixture.⁵ One line only was obtained at 55 which appeared integral with the neighbouring line of Fe^{56} . As the chemical atomic weight 54.93 is in very close agreement with that expected from the packing fraction curve for an atom of this mass number manganese may be safely regarded as a simple element.

43. *Masurium.*

The existence of this element has only been proved so far by its X-ray spectrum. It is extremely rare and difficult to isolate. When a sufficient quantity is available it is hoped to determine its constitution in the same manner as that of its homologue, rhenium.

¹ Aston, *Phil. Mag.*, 42, 141, 1921. ² *Ibid.*

³ Aston, *Proc. Roy. Soc. A*, **115**, 487, 1927.

⁴ Hevesy and Hobbie, *Zeit. anorg. Chem.*, **208**, 107, 1932.

⁵ Aston, *Phil. Mag.*, 47, 396, 1924.

75. *Rhenium.*

This recently discovered element was investigated by **means** of its volatile heptoxide.¹ The way in which its analysis was accomplished is an excellent illustration of the capricious nature of the problem of producing mass rays by means of the discharge tube. The substance, which is a highly hygroscopic crystalline solid, was first treated in the same way as osmium tetroxide, but although a somewhat similar disturbance of the discharge made it clear that doses of the vapour had entered the bulb, yet no rhenium lines were obtained. The solid was then introduced into the bulb itself, as had been selenium and tellurium tetrachloride, but notwithstanding the fact that the distillation was made so copious that a visible layer was formed on the glass walls, still no lines could be seen. At this stage work on the element was abandoned as quite hopeless and preparations were made to proceed to the next. By a piece of remarkable good fortune this happened to be gold which it was intended to attack by means of its slightly volatile chloride. This compound gives off chlorine when heated and as previously it had been noticed that the presence of a halogen gas often stimulated the appearance of lines otherwise faint, it was considered just worth while to make one trial with it *before* the rhenium oxide deposit had been removed from the walls. This procedure was successful beyond all hopes. Although no lines of gold were visible the rhenium doublet appeared in great strength and was repeated 16, 32 and 48 units higher as ReO , ReO_2 and ReO_3 , in this way providing unusually convincing evidence of its isotopic constitution.

The fact that it consists of isotopes 185 and 187 was expected from the general rule that complex elements of odd atomic number (above 9) consist of two odd mass numbers two units apart, but it is of interest as being the first odd element analysed in which the heavier constituent is the more abundant. The ratio of this abundance was established photometrically, by analogy with the mercury lines, to be 1.62. The favourable position of line 203 due to Re^{187}O among those of mercury enabled an estimate of its packing fraction to be obtained with comparative ease. This appears to be -1 ± 2 , the same as that of osmium with which it shares the isobar 187. From these measurements after making the usual corrections we get

$$\text{Atomic weight of rhenium} =? 186.22 \pm 0.07,$$

showing good agreement with Honigsmid's latest value 186.31.

¹ Aston, *Proc. Roy. Soc. A*, 132, 496, 1931.

GROUP VIII

26. *Iron.*

The first results for iron were obtained by means of its volatile carbonyl.¹ They indicated that its principal isotope was of mass number 56. The spectra showed a faint line 54 the origin of which was doubtful owing to the presence of compounds. The existence of the rarer isotope 54 was definitely proved later by means of accelerated anode rays,² and its abundance estimated at about 5 per cent.

Accurate determinations of the packing fraction of iron have not yet been made, but even with the first mass-spectrograph it was possible to conclude that line 56 corresponded to a mass less than an integer by about 1 in 1000. A negative packing fraction of about — 10 is suggested by the curve and brings the data above into good agreement with the chemical atomic weight 55.84.

21. *Cobalt.*

The only work on this element was done with the first mass-spectrograph by the method of accelerated anode rays.³ Anhydrous cobaltous chloride was used in the anode and a single line was obtained corresponding to mass number 59. This result, the chemical atomic weight 58.94 and the value of the packing fraction expected from the curve all agree to make it highly probable that cobalt is a simple element.

28. *Nickel.*

Nickel received attention early in the history of positive rays as it is one of those elements whose atomic weight is out of order in the periodic table ; its atomic weight 58.69 should be greater, not less than that of cobalt 58.84. It is amenable to treatment in the ordinary discharge tube, for it forms an easily vaporizable carbonyl compound $\text{Ni}(\text{CO})_4$. Unfortunately this is 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.

Later by the use of abnormally high current intensities in the discharge it was 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

¹ Aston, *Phil. Mag.*, 45, 940, 1923.

² *Ibid.*, 49, 1198, 1925.

³ *Ibid.*, 47, 395, 1924.

stronger at 58 and the weaker at 60, with a ratio of intensity of about 2 to 1.¹

Measurements of the packing fraction of nickel have been made with the second mass-spectrograph by using the approximate ratios C : CH₄ and CO₂ : Ni⁵⁸. It was difficult to get suitable intensities for good comparison, but the results indicated a value of about — 10. No photometric measurements of the relative intensities of the lines are yet available, but the chemical atomic weight 58.68 is in fair agreement with the rough estimates given above.

44. *Ruthenium.*

Data for this element have only recently been obtained by the use of its volatile tetroxide.² The action of this on the discharge was even worse than that of the corresponding osmium compound,³ and the incidental difficulties attending its use so excessive that it must be regarded as lucky that any useful results were obtained at all. Ruthenium appears to have six isotopes with the possibility of a very faint seventh. Only rough estimates of their relative abundance could be made by photometry. They are :

Mass number	.	.	96	98	99	100	101	102	104
Abundance	.	.	5	?	12	14	22	30	17

These give an isotopic moment of 1.44 and a mean mass number of 101.18.

The packing fraction could not be measured but is probably about — 6 giving an atomic weight on the chemical scale of 101.1. The International figure is 101.7 but is not particularly well established.

45. *Rhodium.*

No suitable volatile compound of rhodium is available and attempts with anode rays have all failed to produce its mass-spectrum. Its chemical atomic weight 102.91 makes it very probable that rhodium is simple of mass number 103.

46. *Palladium.*

No data are yet available on this element.

76. *Osmium.*

This element was recently investigated by means of its tetroxide.² This is a solid sufficiently volatile for use, but the effect of introducing its vapour into the normal discharge is quite amazing. The best

¹ Aston, *Phil Mag.*, 45, 936, 1923.

² Aston, *Proc. Roy. Soc. A*, 132, 487, 1931.

³ *q. v.*

analogy is that of the injection of a violent drug, such as strychnine, into a living organism. The ordinary mechanism of the discharge appears to be completely upset and only slowly recovers. No doubt part of this transformation is due to the decomposition of the compound in the body of the discharge, but in addition the vapour appears to act on the surface of the wax forming the joint between the bulb and the mass-spectrograph, depositing a layer, presumably of osmium, which while fresh behaves somewhat like a Wehnelt cathode. The best way of minimizing these objectionable properties was to admit small doses intermittently while the discharge was being fed with a small leak of CO_2 . By means of long exposures fairly satisfactory spectra were obtained which showed four strong isotopes and two very weak ones, one of which is isobaric with W^{186} .

In order to determine the packing fraction of osmium advantage was taken of the appearance of two lines 206, 208, due to compounds of the two strongest constituents with oxygen. These two lines were sufficiently close to those of mercury for the masses of the groups to be compared. The use of wide slits make the measurements rather rough, but they indicate a value -1 ± 2 .

The relative abundance of the isotopes was estimated by the comparison of the intensities of their lines with those of the mercury group; the percentages are:

Mass number	.	186	187	188	189	190	192
Abundance	.	1.0	0.6	13.4	17.4	25.1	42.5

These give an isotopic moment of 1.40 and a mean mass number of 190.35. After making the usual corrections the atomic weight works out at 190.31, a value considerably lower than the chemical one, 190.8.

77. *Iridium.*

No data for this element are available. Its chemical atomic weight 193.1 is not particularly certain, but if we rely upon it iridium should consist of a main isotope 193 with a smaller quantity of 195.

78. *Platinum.*

Attempts to obtain the anode rays of this element by mixing platinic chloride with the anode paste have all failed, probably owing to its rapid decomposition when heated. A more recent experiment was made by means of a volatile compound $\text{PtCl}_2(\text{CO})_2$. This was treated in the same way as rhenium heptoxide, but gave no platinum lines even when free chlorine was introduced.

PART IV

THEORETICAL AND GENERAL

CHAPTER XIII

THE ELECTRICAL THEORY OF MATTER

94. The Whole-Number Rule.—The first and by far the most important generalization which could be made from the results obtained with the first mass-spectrograph was that the weights of all atoms could be expressed as whole numbers to a high degree of accuracy. This approximation which is called the "whole number rule" enabled the most sweeping simplifications to be made in the ideas of mass and removed the only serious objection to the unitary theory of matter.

95. 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. *Front'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 electrical charges always possess the property of mass, 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. Modern developments of physics carry a warning that this conclusion may not be the whole story, and that other bodies equally primordial may be capable of existence, but very great progress has already been made on the simplest available hypothesis that all matter is built of protons and electrons.

96. 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. It is not proposed to describe its history and properties at any length here. It will be sufficient to note a few of its more important constants.

Its charge e is 4.770×10^{-10} E.S.U. The most reliable measurements of e/m for the electron, at low velocity, give the value 5.28×10^{17} E.S.U. Hence its mass is almost exactly 900×10^{-28} grs., 1845 times less than the mass of the hydrogen atom, or 0000546 on the ordinary scale of atomic weights.

97. 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 1.00724 on the physical scale $O^{16} = 16$, that is about 1.66×10^{-24} grs.

98. The Nucleus Atom.—Certain experimental results, notably the scattering of alpha rays, led Sir Ernest Rutherford in 1911 ³ to formulate an atom model which has resulted in 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 spectra, 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. There is ample literature available on the exterior structure of the atom, that is to say, that part of it consisting of planetary electrons. Modern wave mechanics has been applied to these with striking success so that it is possible, with the aid of the "exclusion principle," to explain how the periodic table is built up. These developments are, however, not necessary to explain the main attributes of isotopes for which the simplest type of Rutherford-Bohr model is adequate.

99. Diagrammatical representation of atoms of Isotopes and Isobares.—The accompanying diagrams (Fig. 29) 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. 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

¹ From Greek *πρῶτον* first—the primary substance.

² P. 100.

•Rutherford, *PHI. Mag.*, 21, 669, 1911.

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

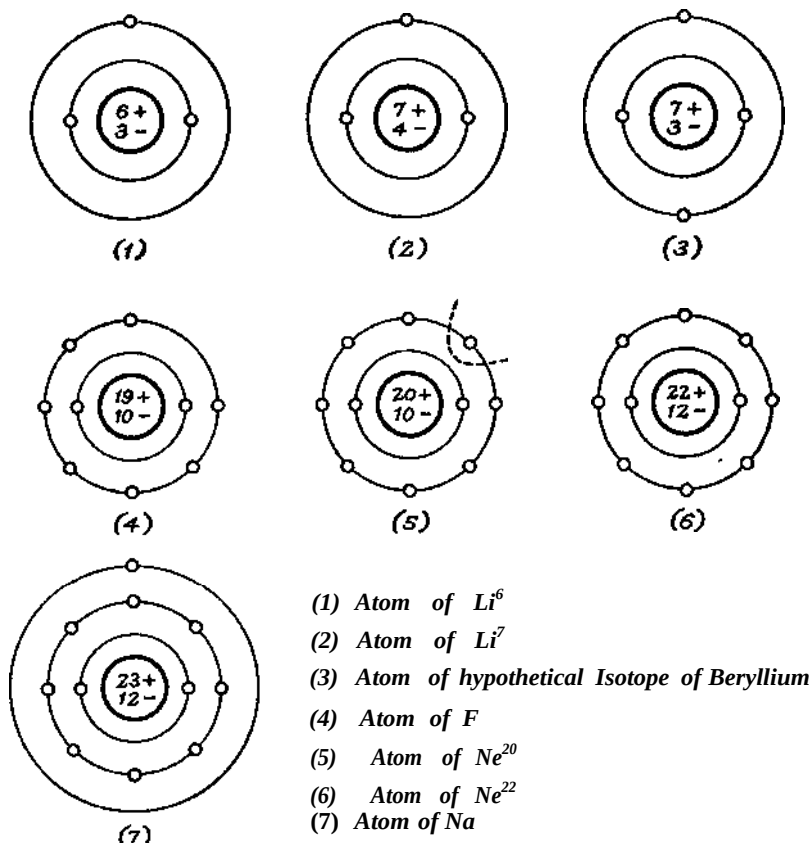


FIG 29.—Diagrammatic Representation of Nucleus Atoms. The planetary electrons are shown as lying on plane circles, the first containing 2, the second 8 and so on. The dark circle is the nucleus and the + and — charges within it are indicated by figures. (1) and (2) are Isotopes. (2) and (3) are Isobares and (5) and (6) are Isotopes.

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.

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

100. 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 the core of the atom lying within the shell of these valency electrons. The movements of the outermost electrons will depend in the first degree on the charge on the core, which may be looked upon as a virtual nucleus. The cores 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 core. Chemical similarity is carried a stage further in the triad groups of the transition elements such as iron, cobalt and nickel. In these not only is the charge on the core the same, but also the construction of the outer shell of the core is closely similar for all these elements. In the group of trivalent rare earths the similarity extends even deeper and the construction of two shells of the core hardly varies within the group so that chemical differentiation is now so feeble that the elements can only be separated from each other with the greatest difficulty. The final stage of similarity is reached in isotopes where the nuclear charge being the same chemical differences vanish for all practical purposes.

101. 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 the outer position, or by sharing the electrons in the atom of another element so that they fill the gaps in its own outer shell. This idea of electron sharing has been of great value 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. We trace the tendency of the atom of fluorine, or any other halogen, to form compounds with the atom of an electropositive element, or with the atom of hydrogen, to the fact that it has one electron too few 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 important idea was first suggested by Sir J. J. Thomson in connection with the charged atoms of chlorine¹ and certainly supplies a very satisfactory explanation of the 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. 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. This behaviour in positive rays should not be entirely unexpected by the chemist, for it is clearly similar to the formation of positively charged ions such as NH_4^+ which are well known in the chemistry of solutions.

102. Failure of the Additive Law with regard to Mass.—For velocities small compared with that of light the masses of the proton and the electron may be regarded as universal constants, and if the additive law of mass held as accurately when an atomic nucleus is built up of them as when, for instance, a molecule is built of atoms the divergences from the whole-number rule would be too small to be significant, and, since a neutral hydrogen atom is one proton plus one electron, the masses of all atoms would be whole numbers on the scale $\text{H} = 1$. The measurements made with the first mass-spectrograph were sufficiently accurate to show that this was not

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

true. The theoretical reason adduced for this failure of the additive law is that, inside the nucleus, the protons and electrons are packed so closely together that their electromagnetic fields interfere and a certain fraction of the combined mass is destroyed, whereas outside the nucleus the distances between the charges are too great for this to happen. The mass destroyed corresponds to energy released, analogous to the heat of formation of a chemical compound, the greater this is the more tightly are the component charges bound together and the more stable is the nucleus formed. It is for this reason that measurements of this loss of mass are of such fundamental importance, for by them we may learn something of the actual structure of the nucleus, the atomic number and the mass number being only concerned with the numbers of protons and electrons employed in its formation.

103. Standard of Mass.—As soon as it was found possible to measure the masses of atoms to a high degree of accuracy it became necessary to decide upon a suitable unit of mass. At the time the first high-precision measurements were made oxygen was regarded as a simple element and its line 16 was very naturally adopted as a standard of reference and the mass corresponding to one-sixteenth of the neutral atom O^{16} was taken as unity.

When the complexity of oxygen was discovered and it became clear that this unit differed from the classical chemical one—one-sixteenth of the mean oxygen atom—the matter had to be reconsidered. At a discussion on the subject at the meeting of the British Association in 1931 it was urged¹ that the chemical standard should remain as before. It gives a scale upon which many of the most frequently occurring elements are sufficiently close to whole numbers for all ordinary calculations of analysis. From the purely chemical view the discovery of the complexity of oxygen is clearly of little importance. The actual sub-standards of atomic weight determination, chlorine, bromine and silver have long been known to be complex to a much more serious degree. As, in all probability, most chemists will be dealing for an indefinite time to come with the present mixed but constant quality of complex elements it seems needless to alter a standard which has figured in chemical literature for so long a time.

For physical purposes it is essential that the unit should be founded on some definite species of atom which can be recorded on a mass-spectrum. Logically the hydrogen atom of mass number 1 would at first sight appear the natural unit, but although this would make all the packing effects of the same sign it is practically inadmissible since it throws the masses of the heavy atoms right off their proper mass

¹ Aston, *Brit. Asa. Report*, 333, 1930.

numbers. $\text{He} = 4$ avoids this defect and is the only possible standard which appears to offer an identical physical and chemical scale.¹ But this appearance can only rest on the unproved assumption that helium is truly a simple element, though the probability is admittedly very high for helium actually derived from radioactive disintegrations. Helium cannot be used as a practical chemical standard for obvious reasons. Its density is not easy to fix and for the purposes of the mass-spectrograph it is too near the low end of the scale. It is questionable if the possible advantages of its adoption would offset the wholesale alteration of all accepted atomic weights, though this has actually been carried out by Gamow.² The only physical data at present available for comparing the masses of atoms with high accuracy are band spectra and mass-spectra. For the former a very high accuracy is claimed, but as they can only be used to compare atoms of the same element with each other the general problem can only be attacked by the mass-spectrograph. For work with this instrument the atom O^{16} is much the most convenient standard for a variety of reasons and is at present in general use. That the chemical and physical scales should differ, and by an amount at present by no means certain, is admittedly unfortunate, but it only seems likely to cause serious inconvenience in exceptional cases, such as the atomic weights of the radiogenic leads.

104. Isotopic Weights and Packing Fractions.—The mass of a neutral atom on the scale $\text{O}^{16} = 16$ is usually called its "isotopic weight" and with the high accuracy now attainable requires at least six figures for its expression. It can be calculated from the results of the mass-spectrograph, but in some respects a more convenient quantity for expressing these, and indeed the quantity which is actually measured, is the percentage difference between the isotopic weight of the atom and its mass number; this is called its "packing fraction." It is the divergence of the atom from the whole-number rule divided by its mass number, the mean gain or loss per proton when the nuclear packing is changed from that of oxygen to that of the atom in question. Expressed in parts per 10,000 it usually requires two, or at most three, significant figures and has much the same experimental probable error in all parts of the scale. Put in another way, if we suppose the whole numbers and the masses of the atoms to be plotted on a uniform logarithmic scale such that every decimetre equals a change of 1 per cent., then the packing fractions are the distances, expressed in millimetres, between the masses and the whole numbers. Fairly accurate data on the isotopic weights and packing

¹ Grosse, *Zeit. f. Phys. Chem.*, 10, 395, 1930.

² Gamow, *Constitution of Atomic Nuclei and Radioactivity*, Oxford, 1931.

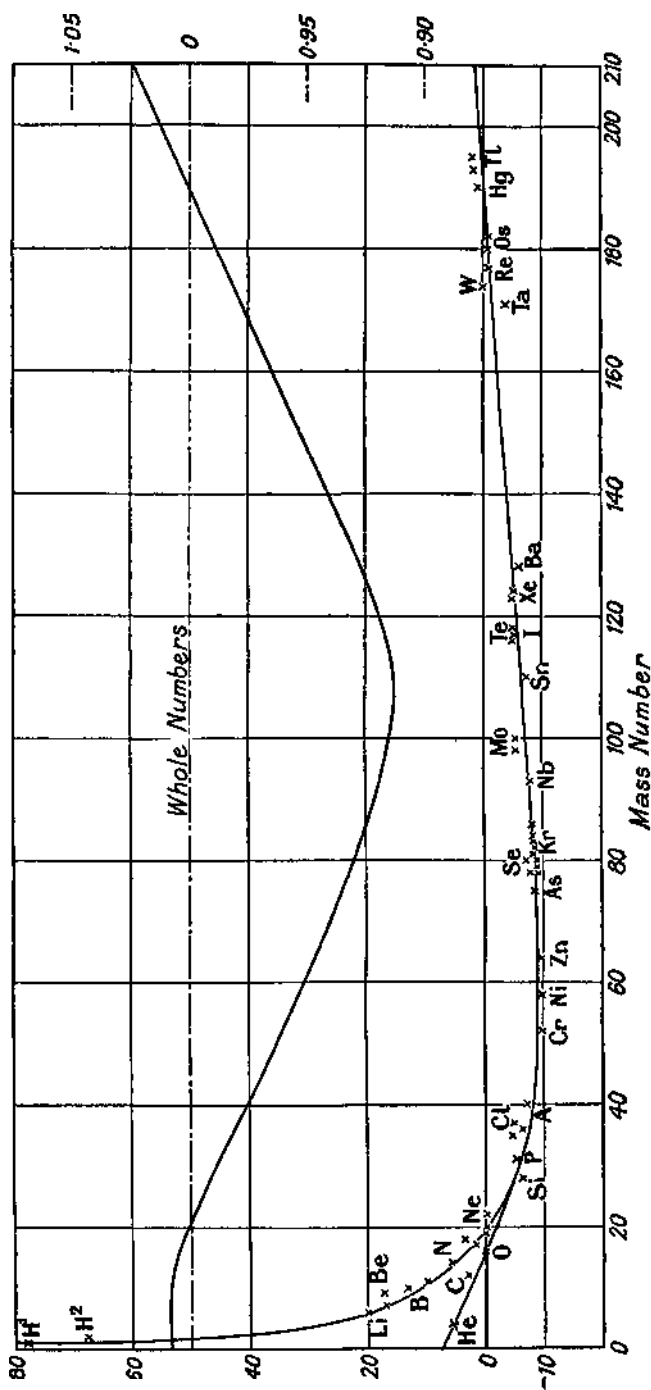


Fig. 30.—Mass Numbers and Packing Fractions.

fractions of some 56 atomic species are known and are given in the Table on page 235.

If we plot packing fraction against mass number as shown in Fig. 30 a very interesting result is obtained. With the exception of the atoms He^4 , C^{12} and O^{16} , of even atomic number, which lie on a side branch, all the others fall roughly on a hyperbolic curve. This descends steeply from hydrogen +77.8 through a zero value in the region of fluorine 19 to a minimum of about -10 near mass number 50 and then rises gradually to recross the zero line near mercury 200. This is called the "packing fraction curve" and by its means the masses of atoms so far not measured can be predicted with fair con-

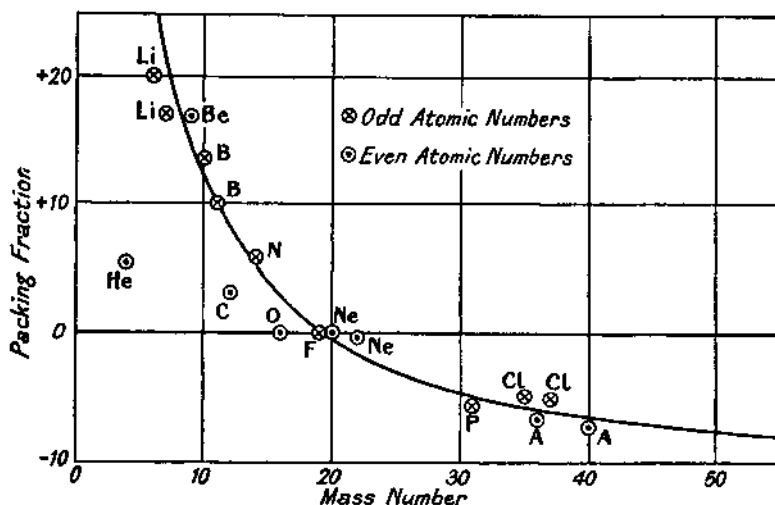


FIG. 31.—Part of Curve of Fig. 30 enlarged to show position of light even-numbered Atoms.

fidence. This curve has been used freely by Millikan and others in theoretical work on the cosmic relations between matter and energy.¹ Its extrapolation beyond mercury is in reasonable agreement with the known data of the radioactive atoms and its slope is sufficient to account for the large amount of energy emitted by them as they disintegrate to atoms of small mass number.²

In Fig. 31 a portion of the curve is shown enlarged to indicate the exceptional position of the light even-numbered atoms. As they lie below the others it follows that their nuclei are more stable, a deduction in excellent agreement with the fact that they are much

¹ Millikan and Cameron, *Phys. Rev.*, 37, 236, 1931.

² Rutherford, *Proc. Roy. Soc. A*, 123, 381, 1929.

more resistant to disintegration by impact of swift particles. The very recently measured value for beryllium shows that this, unlike others of even atomic number, falls nearly on the curve for those of odd number.

The upper curve in Fig. 30 is the approximate result of plotting the actual differences between the isotopic weights and whole numbers. This curve rises to a maximum of 0.015 for beryllium, crosses the whole-number line in the region where the packing fractions are zero and descends to a minimum in the region of tin and then rises again. It is to be emphasized that figures which represent the excess or defect of isotopic weight are not really suitable for plotting in this way as, unlike those representing packing fractions, they have widely divergent experimental errors. The error for mercury, for instance, being 200 times that for hydrogen, so that for heavy atoms the actual values are scattered widely and the curve has little meaning at all. It is of interest to note the position of the minima of the two curves. That of the packing fraction lies in the region of iron, one of the most abundant elements in Nature, while that of defect of mass below a whole number is exhibited in tin, the element which contains the largest number of isotopes yet observed.

105. The Structure of the Nucleus.—It is not proposed to discuss in any detail the innumerable theories for the possible manner in which the electrical charges forming the nucleus are combined, for recent discoveries of the neutron and the possibility of positive electrons have opened the entire field afresh.

From the first the presence of electrons in the nucleus has led to insuperable difficulties. At the time when the electron was regarded as a simple spherical electric charge of definite size it was shown experimentally that the dimensions of the nuclei of heavy atoms were altogether too small to find room for the numerous electrons they were supposed to contain. Later when the wave mechanics was applied other difficulties arose and it was recently concluded by Bohr¹ that theoretical treatment of electrons, as such, in nuclei must be abandoned. The view now in favour is that all the negative electricity inside nuclei must be combined in the form of neutrons or alpha particles.

The first general application of the quantum theory to nuclei is due to Gamow² and Gurney and Condon.³ This theory has been particularly successful in explaining the properties of the radioactive nuclei. For an account of this and of the latest views of the structure

¹ Bohr, Volta Congress, Rome, 1932.

² Gamow, *Zeit. f. Physik.*, 51, 204, 1928.

• Gurney and Condon, *Phys. Rev.*, 33, 127, 1929.

of nuclei in general the reader is referred to the work of Gamow¹ and that of Heisenberg.²

The accurate knowledge of the masses of atoms is clearly of the greatest importance in testing hypothetical nuclear structure. The difference between the mass of the nucleus formed and the total mass of the particles supposed to form it represents the energy released on its formation. This is called the "mass defect" of the nucleus and is a measure of the binding force holding it together. As an illustration, on the hypothesis that the oxygen nucleus consists simply of four alpha particles its mass defect would be 16 times the packing fraction of helium, that is to say 0.00864 on the atomic scale of mass. This figure is a measure of the stability of an oxygen nucleus built in this way. Had the packing fraction of helium proved to be zero or negative such a construction could have been ruled out at once as impossible since no binding energy would be available.

The mass defects of some of the lighter nuclei have been estimated from recent observations on artificial disintegration and other phenomena of nuclear collisions and agree fairly well with those deduced from packing fractions.³

106. Transmutation and Atomic Energy,—Two results which were first demonstrated by the mass-spectrograph, firstly the whole-number rule, which showed the high probability of all atoms being composed of the same ultimate units, and secondly the fact that one helium atom does actually weigh less than four hydrogen atoms have profound and far-reaching theoretical implications.

We know from Einstein's Theory of Relativity that mass and energy are interchangeable 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. 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 transmuted into helium the energy liberated will amount to about 6.5×10^{18} ergs or 200,000 kilowatt hours. This transformation of

¹ Gamow, *Constitution of Atomic Nuclei and Radioactivity*, Oxford University Press, 1931.

² Heisenberg, *Zeit. f. Physik.*, 78, 156, 1932.

³ Chadwick, *Proc. Roy. Soc. A*, 130, 463, 1931 ; *A*, 136, 692, 1932.

mass into radiation by the partial or complete annihilation of matter is the so-called "atomic energy" believed to be the source of the heat of the stars and which, it was predicted, might be tapped and used when a means of artificial transmutation of elements was discovered.

That this was not merely an idle fancy is now clear, for already in the last two years artificial transmutation has become an accepted fact. Cockcroft and Walton¹ were able to demonstrate that lithium under the impact of swift protons disintegrated, giving off alpha rays, and that these rays possessed an energy enormously greater than that of the proton effecting the change. The ranges observed and the energies calculated from the relative packing fractions of hydrogen and lithium agree well with the view that a proton, crossing the potential barrier according to the theory of Gamow, is able to enter the nucleus of an atom of Li^7 resulting in the formation of two alpha particles which are ejected simultaneously. Other light elements have also indicated possibilities of similar transmutations. Though it must not be forgotten that a probability factor of a high order cuts down the total energy liberated in this way to a minute fraction of that in the stream of protons employed, the first step has been taken, and as it is now being eagerly followed up in laboratories all over the world rapid developments may be confidently expected.

¹ Cockcroft and Walton, *Nature*, 129, 649 ; *Proc. Roy. Soc. A*, 137, 229, 1932.

CHAPTER XIV

ISOTOPE STATISTICS

107. The relation between chemical atomic weight and atomic number.—The importance of the chemical atomic weight has been greatly reduced by the discovery of isotopes as it is now recognized to be in general merely a statistical mean value. 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 ever.

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. 32) 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.

108. Statistical relations exhibited by elements and their isotopes.—Of some 84 elements existing in workable quantity 66 have been analysed and of these 20 appear to be simple. Interesting relations of various kinds have been noted among the many species of atoms disclosed. These are illustrated in the diagram Fig. 33 in which all the known mass numbers are given in order. Some of the more important relations may be 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 rule. 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. Mass numbers corresponding to $2N$ are known in the majority of the lighter elements up to Ca^{40} . 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 case of mercury it amounts to 37 units. The corresponding divergence of the *mean*

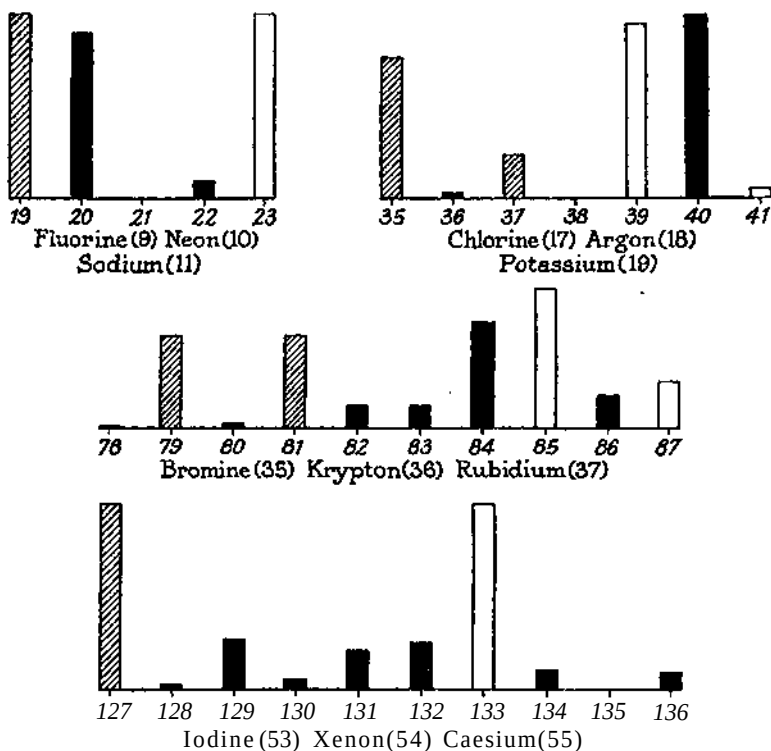


FIG. 32.—Isotopes of the Halogens, the Inert Gases and the Alkali Metals.

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 mass number 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. The largest number known with certainty is eleven in the case of tin. This is followed by xenon, mercury and ordinary lead with nine each. The maximum difference between the lightest and

H	He																	Li	Be	B	C	N	O	F	Ne	Ne	Ne
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22						
																		Ca									
Na	Mg	Mg	Mg	Al	Si	Si	Si	P	S	S	S	Cl	A	Cl				K	A	K			Ca				
23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44						
										Cr																	
Sc				Ti	Cr	V	Cr	Cr	Fe	Mn	Fe				Ni	Co	Ni				Cu	Zn	Cu	Zn			
45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66						
				Ge					Ge	Ge	Kr	Kr	Kr					Sr	Sr								
Zn	Zn	Ga	Zn	Ga	Ge	Ge	Se	As	Se	Se	Se	Br	Se	Br	Se	Kr	Kr	Rb	Kr	Rb	Sr						
67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88						
										Ru																	
				Mo	Mo	Mo	Ru	Ru									Ag	Ag	Cd								
Y	Zr			Zr	Nb	Zr	Mo	Zr	Mo	Mo	Ru	Mo	Ru	Ru				Ru				Ag	Ag	Cd			
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110						
														Tc													
				Sn	Sn	Sn	Sn					Sn	Te	Te	Xe	Xe	Xe	Xe									
Cd	Cd	Cd	Cd	In	Cd	Sn	Sn	Sn	Sn	Sb	Sn	Sb	Sn	Te	Te	I	Te	Xe	Te	Xe	Xe						
111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132						
										Ba					Nd												
Cs	Xe	Ba	Xe	Ba	Ba	La	Ce	Pr	Ce	Nd	Nd																
133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154						
155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176						
										Os	Os																
				Ta	W	W	W	Re	W	Re	Os	Os	Os				Os					Hg	Hg	Hg			
177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198						
				Pb					Pb	Pb	Pb					Pb											
				Tl	Pb	Pb					Pb	Bi	Pb														
Hg	Hg	Hg	Hg	Hg	Hg	Hg	Tl	Pb	Pb	Pb	Bi	Pb											An	Tn			
199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220						
				Rn	Th	Ra	Ac					Lo	Pa	Th	UX					U							
221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242						

FIG. 33.—The first 242 Natural Numbers showing those occupied by Mass Numbers of Known Elements.

the heaviest isotope is twelve units in the cases of tin and xenon. If this is expressed as a proportional difference and we neglect the exceptional cases of hydrogen and lithium there is an exceedingly-curious tendency for the spread of the isotopic groups to approximate to a limit of 10 per cent., as with boron, neon, argon, krypton and tin.

Elements of odd atomic number never have more than two isotopes. This rule is perhaps the most remarkable of all and so far it has no exception. Beyond atomic number 9 the mass numbers of the isotopes always differ by two units and, except in the cases of rhenium and thallium, the lighter is the more abundant.

The number of electrons in the nucleus tends to be even. This rule expresses the fact that in the great majority of cases even atomic number is associated with even mass number and odd with odd. This is clearly indicated in the following table :

	Number of Elements.	Odd Mass Number.	Even Mass Number.	Total Isotopes.	Average Number of Isotopes.
Odd At. No. . .	32	42	4	46	1.31
Even At. No. .	34	39	106	145	4.27
	66	81	110	191	2.9

Further, the mass numbers not obeying this rule are all those of weak isotopic components with the exception of Be^9 , N^{14} and Xe^{129} . Beryllium and nitrogen are the only elements consisting almost entirely of atoms whose nuclei contain an odd number of electrons.

Isobaric pairs and triplets.—Isobares, that is to say atoms having the same mass number but different atomic numbers, are now known in considerable and increasing numbers. In the early work many were overlooked, for in general one at least is a rare type. It will be noticed that in the majority of cases the atomic numbers of the elements forming the pairs are even and differ in each case by two units, and that the common mass number is also even. The most remarkable and important pair is argon calcium, which was the first to be discovered. This is unique in that it consists of the two preponderant isotopes of its constituent elements. These, so far from being particularly rare in Nature, are actually the most abundant inert gas and alkaline earth respectively.

Isobares of odd mass number are very rare, 115 and 123 seem, however, quite certain. The first isobaric triplet discovered was that at 96, but of this the zirconium member is still doubtful. That at

124 seems well authenticated, but the lead and mercury members of the one at 203 are extremely rare and still a little uncertain.

Isotopic Number.—The difference between the mass number of an atom and twice its atomic number has been called by Harkins the "isotopic number" of the atom, it is 0 for many of the light atoms and rises to a maximum 54 which is the value he allots to uranium. He has discussed the relation between natural abundance and isotopic number¹ and shows that atoms of isotopic number 0, such as C¹², O¹⁶, Mg²⁴, etc., predominate in a marked degree. Abundance is much less for isotopic number 1 such as F¹⁹, Na²³, Al²⁷, decreases again for 2:—N¹⁴, Ne²², and becomes practically zero for 3:—Cl³⁷. Later² he gave a valuable table of known and hypothetical isotopes. This is in the form of a diagram in which the isotopic numbers of all atomic species known and probable against their atomic numbers are plotted. They lie on a band of roughly parabolic curvature which widens as it gets further from the origin. The probable constitutions of elements, not experimentally analysed at the time the scheme was drawn up, are admittedly speculative and dependent on the trustworthiness of chemical atomic weight determinations.

109. Periodic Systems of Nuclei.—The extra-nuclear properties of atoms, that is to say their chemical and spectroscopic ones, have enabled them to be classified in the well-known Periodic Table of the elements the numerical relations of which are now well understood and explained. No such table can yet be formulated to express the purely nuclear properties of atoms. Of these properties only one, that of radioactivity, has been adequately investigated and this is only shared by a few of the heaviest types of atom.

The study of isotopes has revealed only one definite periodicity, the apparent limit of the number of isotopes of odd elements, but the significance of this is as yet unexplained. Examination of the mass numbers tabulated on page 174 shows an extraordinarily large number of cases in which a difference of mass number 44 is connected with a difference of atomic number 18 to give atoms having similar chemical properties such as Cl³⁵ Br⁷⁹. In the same way in the longer period 88 is connected with 32 as with Nb⁹³, Ta¹⁸¹.

A great many types of tabulation of mass numbers have been suggested by different investigators as a means of exploration and to suggest possible new isotopes. The work of Harkins has already been mentioned. Russell³ endeavoured to associate, in occurrence

¹ Harkins, *Nature*, 107, 202, 1921.

² Harkins, *Journ. Franklin Inst.*, 194, 645, 1922; *J. Amer. Chem. Soc.*, 45, 1426, 1923.

³ Russell, *Phil. Mag.*, 47, 1121; 48, 365, 1924.

and abundance, all known types of atoms with those formed in known and hypothetical radioactive disintegration series. More recently a scheme devised by Urey¹ led him to search for isotopes of hydrogen and Johnston² by a tabulation dividing mass numbers into groups $4n$, $4n + 1$, $4n + 2$, $4n + 3$, has predicted many new species. A few of these have since been discovered, but in connection with selenium he is quite definitely wrong, as was Russell in predicting that molybdenum would be simple.

An empirical attempt has been made to show a periodicity in the packing fractions of atoms corresponding to their chemical properties but without much success.³ There is no doubt of the connection between the exact masses of atoms and their nuclear structure, but the accuracy of measurement will have to be increased considerably before it will afford any criterion for theory.

110, The relative abundance of elements.—The great disparity in the abundance of different elements in terrestrial and other cosmic matter has long been a problem of the greatest interest and is one of the few possible sources of information for formulating theories of the evolution of the elements themselves. An enormous number of chemical analyses of igneous rocks and other geological material have been accumulated in the past and the results tabulated. During the last decade, however, the much more powerful and convenient method of X-ray analysis has been applied by Hevesy, Noddack and others to the problem with noteworthy success. It is now found that the estimates of the rarer and less-known elements are in most cases much too low, no doubt owing to the extreme difficulty of separating and estimating them by purely chemical methods. For a complete account of the latest conclusions on the abundance of elements in terrestrial and stellar matter the reader is referred to the recent work of Hevesy.⁴

The most obvious points to be noticed in tables of abundance are that the heavier elements are much more rare than the lighter ones and, as was first pointed out by Harkins,⁵ that elements of even atomic number predominate to a very marked extent not only in the earth's crust, but also in such extra-terrestrial matter as meteorites. Harkins' rule is beautifully illustrated by the relative abundance of the rare earth elements as determined by X-ray analyses.

¹ Urey, *Jour. Amer. Chem. Soc.*, 53, 2872, 1931.

² Johnston, *Jour. Amer. Chem. Soc.*, 53, 2866, 1931; 54, 824, 1932.

³ Meyer, *Sitz. Akad. Wiss. Wien.*, **138**, 431, 1929.

⁴ Hevesy, *Chemical Analysis by X-rays and its Applications*, McGraw-Hill, New York, 1932.

⁵ Harkins, *Jour. Amer. Chem. Soc.*, 39, 856, 1917.

Clearly the greatest difficulty in obtaining numerical values of relative abundance which may be used for theoretical purposes is that of defining a fair sample. The Earth taken as a whole may possibly be such, but since the vast mass of its interior is inaccessible, and processes of physical and chemical segregation of the elements have been going on presumably ever since it separated from the Sun, it cannot be regarded as a satisfactory one.

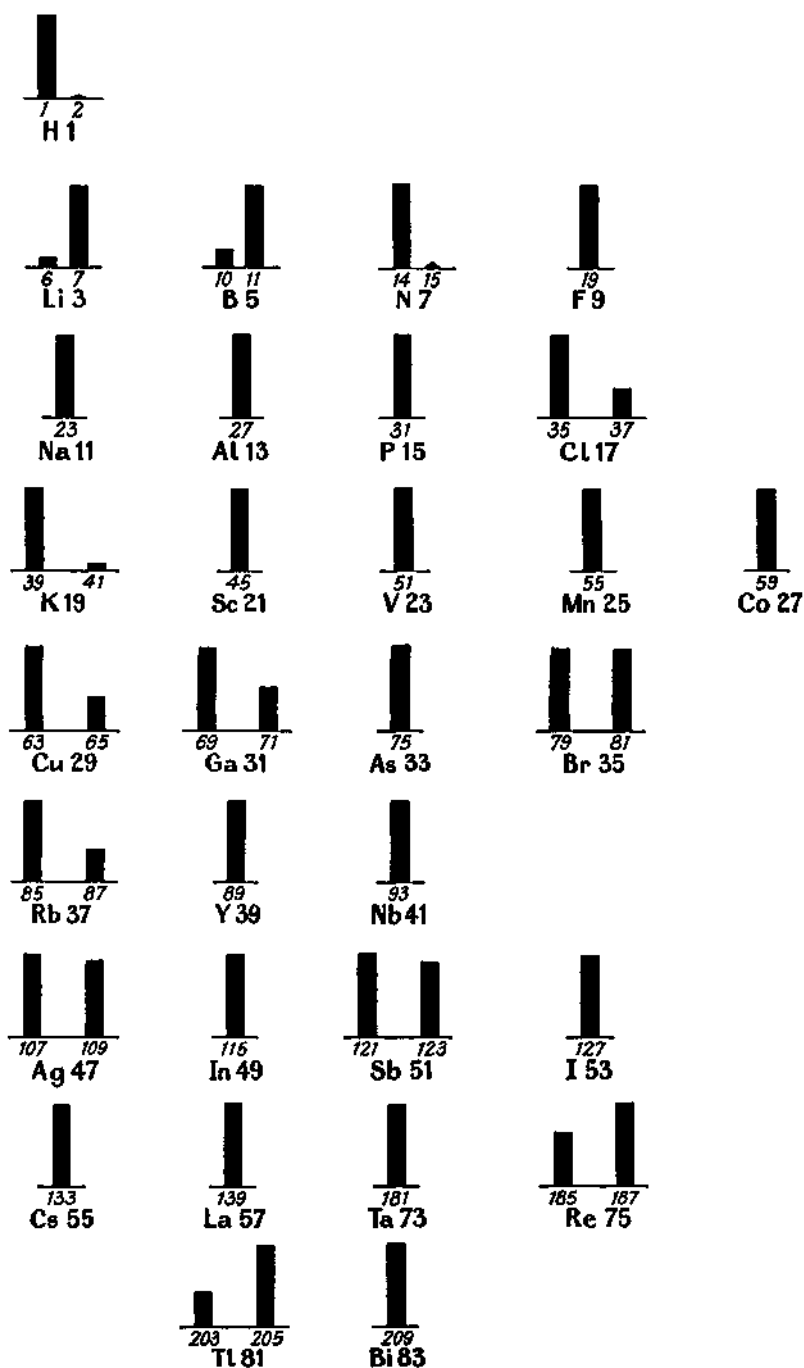
111. The relative abundance of isotopes.—In contradistinction to the chemical problem the determination of the ratios of abundance of constituents of the same element by the mass-spectrograph is virtually free from the uncertainty of sampling. Since the discovery of isotopes among the inactive elements hundreds of analyses have been performed to test the unvarying nature of the atomic weights of naturally occurring complex elements, and, with the possible and numerically insignificant exception of boron, all have given consistently negative results. Only in the laboratory has variation in abundance of isotopes been achieved, and that with immense labour and to a very small degree.

We may therefore say briefly that whereas it is impossible to obtain a mixture of elements which we may regard as a fair sample of cosmic matter it is very nearly as impossible to obtain a mixture of isotopes which is *not* a fair sample of a complex element.

There was therefore a slight hope that systematic measurement of these ratios might reveal relations of fundamental interest. On this account, and also incidentally to check chemical atomic weights, by purely physical methods, the problem was attacked by the methods of mass-spectrum photometry (see Chapter IX).

At the outset the numerical results appeared promising. The very close equality of Kr^{82} , Kr^{83} and to a less degree of the two strongest and two weakest isotopes of xenon seemed possibly significant, also the identity of the ratios $\text{Kr}^{84}/\text{Kr}^{83}$, $\text{Kr}^{84}/\text{Kr}^{82}$ and $\text{Kr}^{82}/\text{Kr}^{80}$ was noted. But as results were accumulated this hope was seen to be unfounded. A complex element with n isotopes yields $\frac{1}{2}n(n+1)$ ratios of abundance and actually well over 250 are available. Tabulation of these has so far failed to show any closer groupings than would be expected from pure chance.

The results of the measurements have already been given for each individual element in Part III and will be found tabulated in Appendix II. They are reproduced in a graphical manner in Figs. 34 and 35. Here the heights of the columns indicate the proportion of each isotope present, the most abundant one being represented as a fixed height as a standard of comparison. Abundance of less than 2 per cent, of the standard is too small for this form of repre-



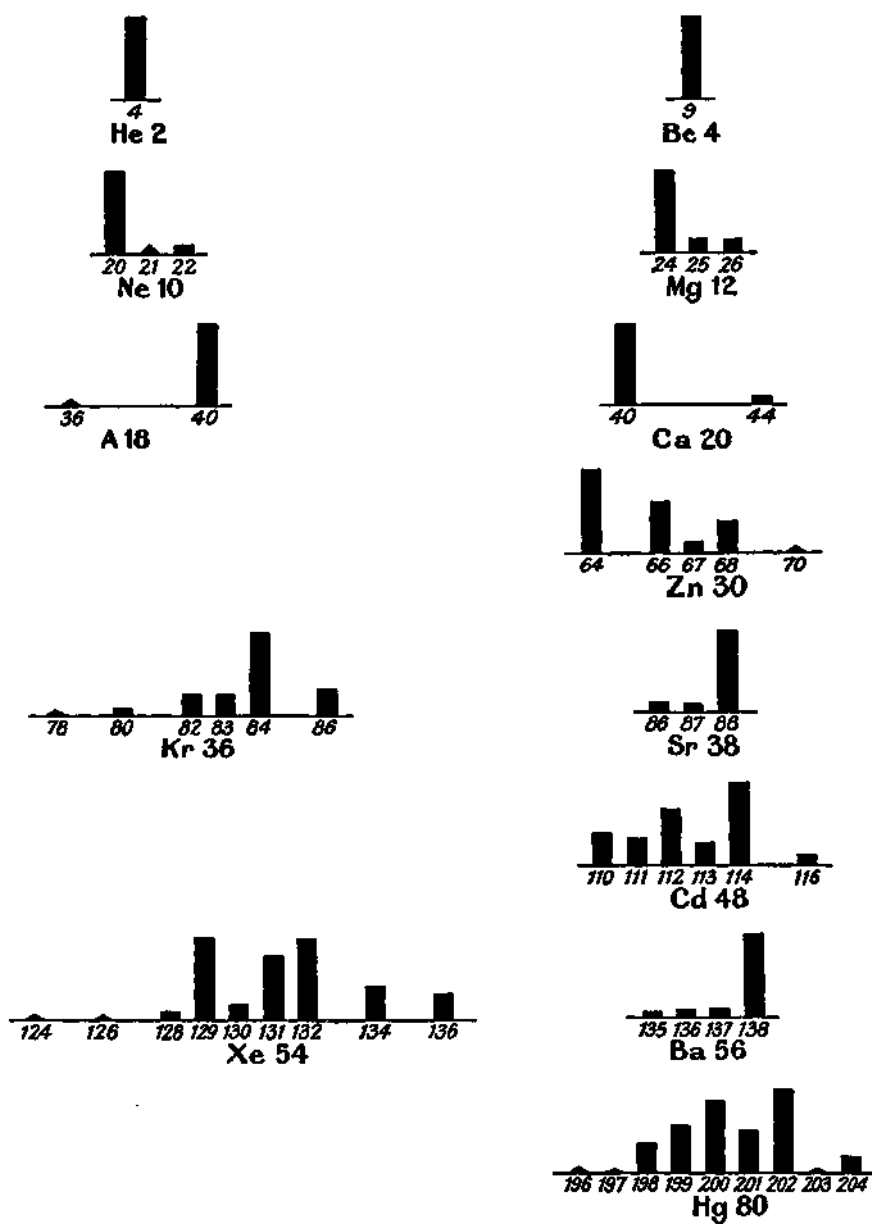


FIG. 35.—Isotopes of Even Elements.

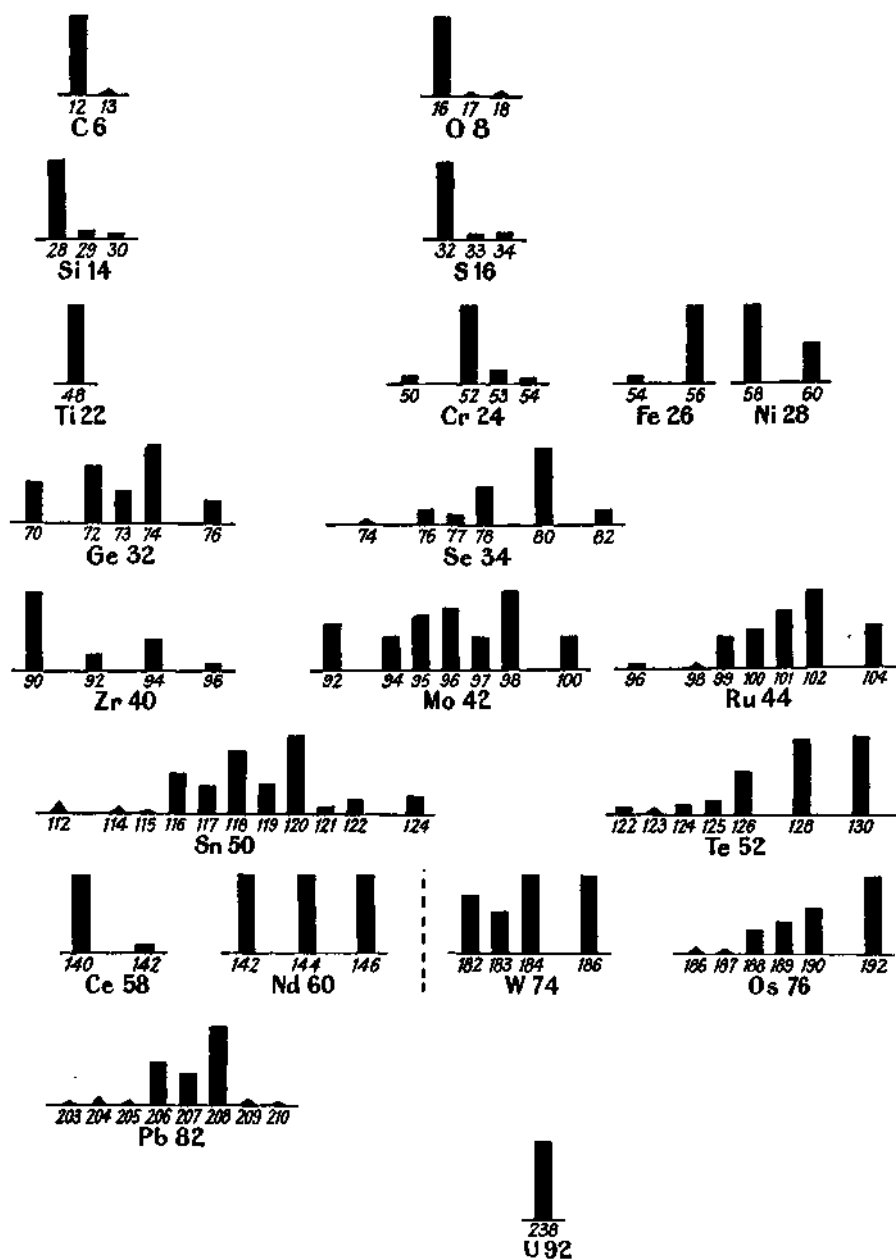


FIG. 35.—Isotopes of Even Elements.

sentation and the occurrence of rare isotopes is indicated by triangles. The height of these has little significance except to indicate which of two mass numbers is the more abundant in the same element. For convenience of printing the odd elements are reproduced separately from the more complex even ones.

In such a form of nuclear periodic table the eye cannot fail to note many interesting and suggestive facts such as the very marked contrast between argon and calcium. There is clearly a family likeness between many of the more complex groups, the abundance growing towards the median mass numbers and then fading away again. In contrast there is the unique group of zinc with its lightest isotope the most abundant, and the remarkable rarity of the lighter isotopes of tellurium and barium. The importance of the differences 44 and 88, already mentioned in connection with mass numbers, is brought out in a most remarkable manner by the series of clusters magnesium, zinc, cadmium and mercury, and only a little less so in silicon, germanium, tin and lead.

112. The abundance of different atomic species on the earth.—In the diagram Fig. 36 the results for the relative abundance of isotopes are combined with Hevesy's values for the elements in igneous rocks to show the relative numbers of atoms of various species present on the earth. Against the mass number of each species is plotted the logarithm to base 10 of the total number of gramme-atoms on the earth. This figure is arrived at in the following manner. The earth is assumed for the purposes of this calculation to consist of a lithosphere of mass 5.98×10^{27} grs. having the average composition of the igneous rocks, a hydrosphere of mass 1.45×10^{24} grs. of water, and an atmosphere of mass 5.29×10^{21} grs. of ordinary air. That the unknown interior of the earth has the same chemical composition as the deeper parts of its outer crust is of course improbable, but to leave it out of the calculation altogether might give the hydrosphere and atmosphere undue prominence.

The types belonging to odd and even atomic numbers are distinguished from each other and those belonging to the same element are joined by lines. In addition to the preponderance of atoms of even atomic number that of mass numbers of type Sn will also be noted.

One point of obvious interest brought out is the extraordinary scarcity of the inert gases. As compared with other elements their abundance on the earth appears to be nearly a million times too small. It is difficult to resist the conclusion¹ that this abnormality must in some way be connected with the absence of any properties enabling them to be fixed in chemical combination.

¹ Aston, *Nature*, **114**, 786, 1924.

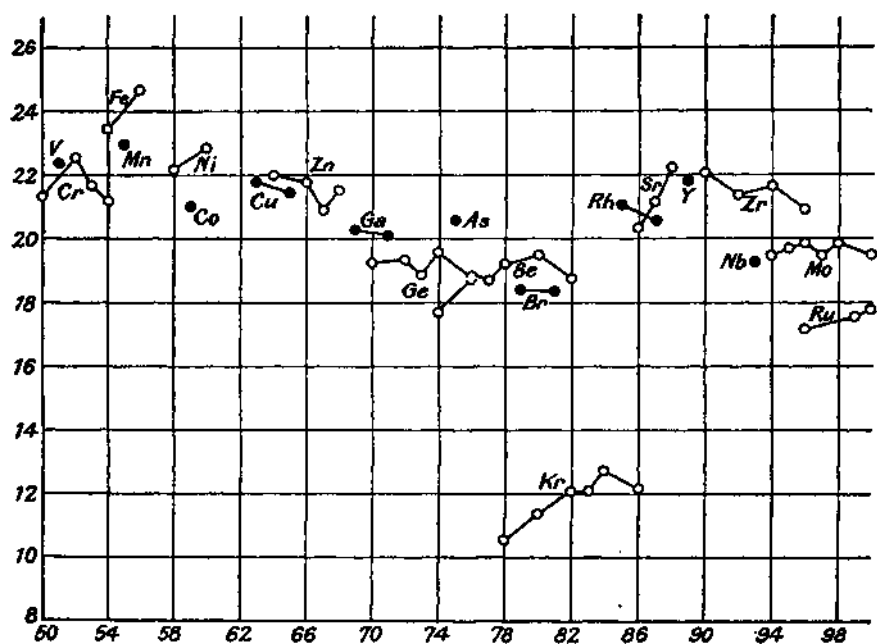
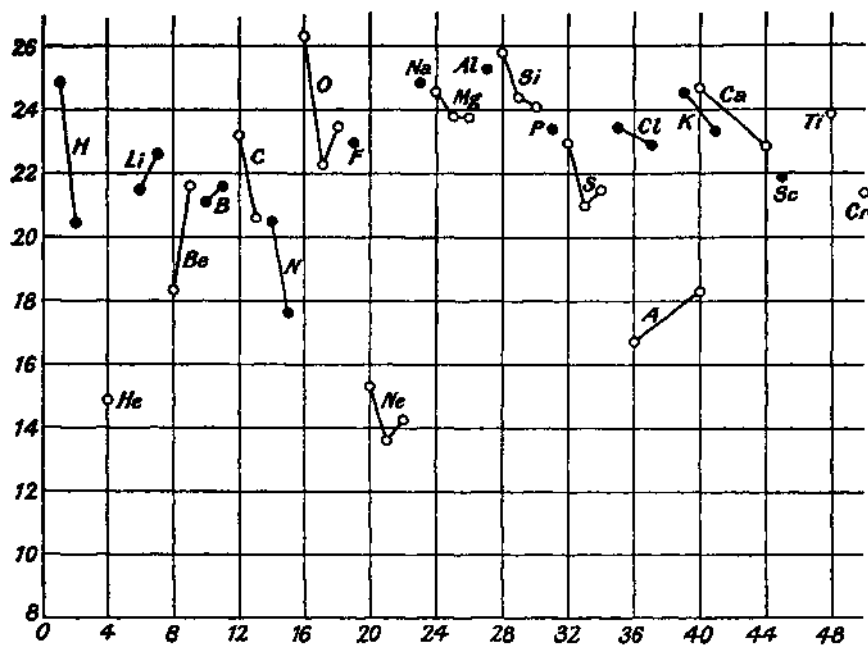
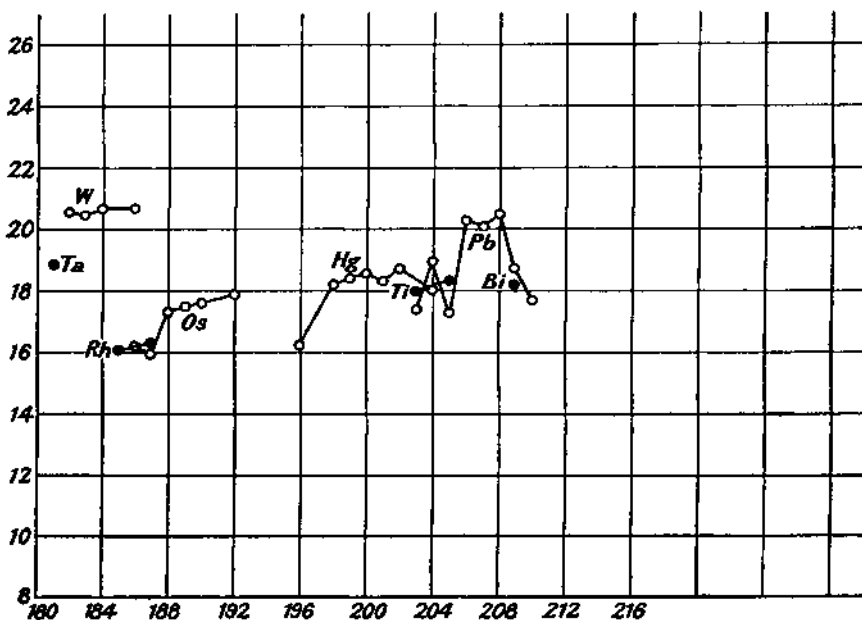
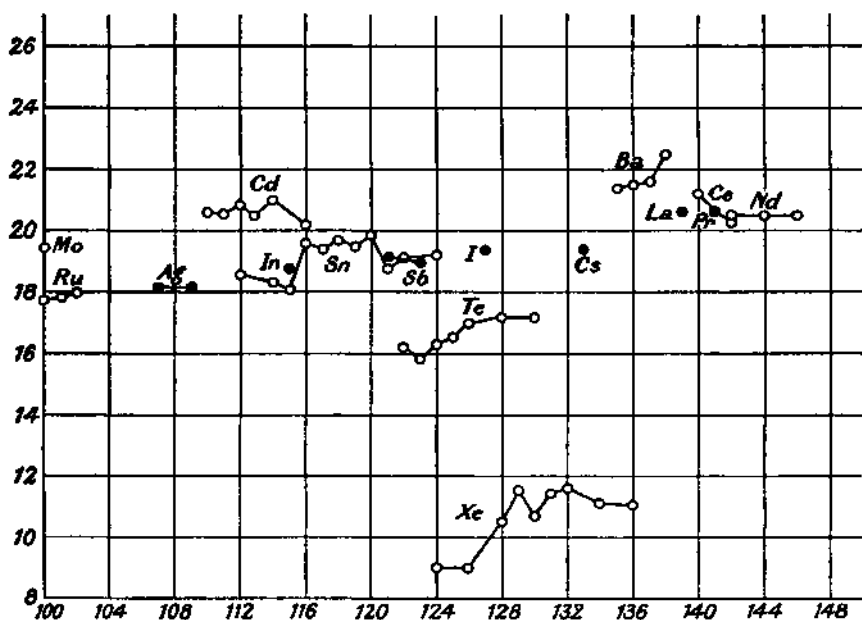


FIG. 36.—Diagram showing the Relative
O Even atomic number.



Abundance of different Atomic Species in the Earth.

• Odd atomic number.

114. 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 was met, in the first place, by the argument 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 extraordinarily 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 soon received 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. Mile Irene Curie¹ 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 seawater. The value 35.60, for chlorine from a sample of sodium chloride from a desert region in Central Africa was slightly high.

Later very careful investigations were made by Mile Ellen Gleditsch and B. Samdahl² on chlorine in an apatite from Oodegaarden in Bamle, Norway. This mineral is found in lodes and the investigators were confident that it was formed from the primary magma and had never been in contact with water. Atomic weight determinations showed no difference between this chlorine and that from ordinary sources. In further confirmation Margot Dorenfeldt³ compared the specific gravities of saturated solutions of sodium chloride made from the apatite material with similar solutions of the ordinary salt. When all corrections had been made, the ordinary chloride gave a figure 1.202867 as compared with 1.202855 for the apatite chloride. The quantity of dry sodium chloride from equal volumes of the solutions was 3.31262 for ordinary, and 3.31267 for the Bamle sample. The differences are insignificant. More recently chlorine has been again

¹ 1. Curie, *Compt. Rend.*, **172**, 1025, 1921.

² Gleditsch and Samdahl, *Compt. Rend.*, **174**, 746, 1922.

³ Dorenfeldt, *Jour. Amer. Chem. Soc.*, **45**, 1577, 1923.

examined by Gleditsch,¹ Harkins and Stone,² and Menzies,³ **but** although very wide ranges of terrestrial and meteoric sources were used no variation was detected.

The comparison of the atomic weights of elements from meteorites with those of terrestrial ones is of particular interest in this connection. The first work of this kind was done on iron by Baxter and Thorvaldson⁴ before the discovery of isotopes. No difference in atomic weight was detected.

A comparison of the atomic weights of terrestrial and meteoric nickel made by Baxter and Parsons,⁵ whilst three experiments with meteoric nickel gave 58.68, as a mean of nine determinations with the terrestrial material the figure 58.70 was found. The standard value found by Richards and Cushman was 58.68. The difference found between terrestrial and meteoric nickel was considered to be within the limits of experimental error. On repeating this work with the aid of the most refined methods Baxter and Hilton⁶ found identically the same value 58.70 for meteoric and terrestrial nickel.

Boron, which has the highest constant of separability, is the only element which has given fairly well substantiated evidence of variation in nature. Although Munro⁷ could detect none Briscoe and others⁸ have reported variations detected both by atomic weight determinations and also by density measurements. The figures are not large; their later report indicates a real difference of about 0.01 of a unit in the mean atomic weight of boron from California and from Asia Minor.

A most important and conclusive paper on the subject is that of Jaeger and Dijkstra.⁹ They worked on the element silicon, which has as wide a distribution in Nature as any complex element and examined it by determining the density of tetraethylsilicane made from it by the Grignard reaction. After carrying out this operation with silicons from six different cosmic and six different terrestrial sources, they found no difference of density greater than 0.0006 per cent. By further investigation they were able to show conclusively that even these small differences were to be attributed to the presence

¹ Gleditsch, *J. Chim. Physique*, **21**, 456, 1924.

² Harkins and Stone, *Proc. Nat. Acad. Sci.*, **11**, 643, 1925; *Jour. Amer. Chem. Soc.*, **48**, 938, 1926.

³ Menzies, *Nature*, **116**, 643, 1925.

⁴ Baxter and Thorvaldson, *Jour. Amer. Chem. Soc.*, **33**, 337, 1911.

⁵ Baxter and Parsons, *Jour. Amer. Chem. Soc.*, **43**, 507, 1921.

⁶ Baxter and Hilton, *Jour. Amer. Chem. Soc.*, **45**, 694, 1923.

⁷ Munro, *Trans. Chem. Soc.*, **121**, 986, 1922.

⁸ Briscoe, *Jour. Chem. Soc.*, **127**, 696, 1925; 282, 1927.

⁹ Jaeger and Dijkstra, *Zeit. Anorg. Chem.*, **143**, 233, 1925.

of traces of by-products too small to be detected chemically. They conclude that terrestrial and meteoric silicon give products not differing by more than the error of experiment which was 000004 per cent.

Of other elements mercury,¹ antimony,² copper,³ and nitrogen⁴ have all failed to show measurable variations.

The accumulation of negative evidence of this kind is impressive, and supports the idea already put forward by the writer⁵ that the evolution of the elements must have been such as to lead to a proportionality of isotopes of the same element which was constant from the start, and, since we know of no natural process of separation, has remained constant ever since. The isotopes of lead formed by radioactive disintegration are exceptional. These substances have been produced continuously during the history of the earth's crust and are being so produced to-day. Although the principal isotopes of ordinary lead may be identical in every respect with those produced in the last stage of radioactive disintegrations, yet there is no particular reason 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

115. The Agreement between Chemical and Physical atomic weights.—The development of methods of measurement of the masses and relative abundance of isotopes enabled chemical atomic weights to be checked for the first time by purely physical means. The atomic weights deduced from determinations of the densities of gases are of course to be included among the chemical ones, for they depend on processes of purification which are essentially chemical.

The early results with the first mass-spectrograph were in agreement with those already obtained by chemical methods. Not only did the masses of oxygen, carbon, helium and nitrogen, assumed to be simple elements, agree with accepted values, but the isotopes of the complex elements neon, chlorine and argon were found to obey the "whole-number rule" and, from a rough estimate of the relative intensity of their lines, appeared to be present in the proportion expected from their chemical atomic weights. Of still greater interest was the discovery that the mass of the hydrogen atom when compared with helium and oxygen was not a whole number but corresponded with the well-established chemical value 1.008,

The first serious discrepancy was noted in the case of krypton,

¹ Bronsted and Hevesy, *Nature*, **109**, 813, 1922.

² McAlpine, *Jour. Amer. Ghent. Soc.*, **51**, 1745, 1929.

³ Phillips, *Jour. Amer. Chem. Soc.*, **51**, 400, 1929.

⁴ Cady and Beecher, *Science*, **68**, 594, 1928.

⁵ *Isotopes*, 1st ed., 113, 1922.

which gave a group of six lines corresponding to masses definitely integral, but when the position of the centre of gravity of this group was estimated it gave a value for the mean atomic weight of 83.5 ± 0.3 . The accepted International figure deduced from the density was 82.92. On the other hand, the relative intensities of the boron lines 10 and 11 suggested a value less than the chemical one, 10.90, then in use. Xenon when analysed gave an estimated mean weight 131.3 ± 0.3 (Intl. 130.2), showing a discrepancy similar to that of krypton. The most glaring case was antimony, which gave two lines of almost equal strength 121, 123, whereas the chemical value 120.2 was still in use. The chemical figure 91 for beryllium was not in agreement with the positive ray evidence that this was essentially a simple element. Revision of the chemical atomic weights reduced to small values the discrepancies in the cases of boron, beryllium and antimony, but those of krypton and xenon remained.

In all these cases the relative abundance of the isotopes was estimated visually from the appearance of the lines on their mass-spectra. The first actual measurements of relative abundances were made by Dempster who, by assuming the whole-number rule, was able to show that the isotopic constitutions of magnesium, potassium, calcium and zinc were in fair accord with their chemical atomic weights.

The construction of the second mass-spectrograph and the development of methods of photometry brought the accuracy of the physical method up to 1 or 2 parts in 10,000, a precision comparable with the best chemical practice. About the same time the discovery of the complexity of oxygen revealed that the scales used were not identical. The International value adopted at present for the conversion of the physical scale $O^{16} = 16$ to the chemical scale $O = 16$ is 1.00022 based on Mecke's estimate of the abundance of O^{17} and O^{18} .

In Table II the atomic weights arrived at by photometry of mass-spectra corrected to the chemical scale by the subtraction of 2 parts in 10,000 are compared with the present International values.¹

It will be seen that the high values for krypton and xenon suggested by their first mass-spectra have been confirmed by the more accurate ones made later and also by the revision of their International values from the latest density determinations. In the case of selenium the most recent chemical result is in exact agreement with that derived from the mass-spectrum.² Scandium, niobium and tantalum are shown by their mass-spectra to be essentially simple and there seems little doubt that their chemical atomic weights are too high. Phosphorus and caesium show discrepancies for which it is

¹ Aston, *Jour. Chem. Soc.*, 2888, 1932.

² V. p. 145.

TABLE II
CHEMICAL AND PHYSICAL ATOMIC WEIGHTS

Element.	Atomic Number.	Inter-national Atomic Weight.	Physical Atomic Weight.	Element.	Atomic Number.	Inter-national Atomic Weight.	Physical Atomic Weight.
H	1	1.0078	100761	Sr	38	87.63	87.64
He	2	4002	400136	Nb	41	93.3	92.90
Li	3	6.940	6.936	Mo	42	960	95.97
B	5	10.82	10.803	Ru	44	101.7	(101.1)
C	6	1200	120037	Sn	50	118.70	118.71
N	7	14008	14.008	Sb	51	121.76	121.78
O	8	16000	16.000	Te	52	127.5	127.58
F	9	1900	18.996	I	53	126.92	126.91
P	15	3102	30.98	Xe	54	131.3	131.26
Sc	21	4510	44.96	Cs	55	132.81	132.91
Cr	24	5201	52.01	Ba	56	137.36	137.42
Zn	30	65.38	65.33	Ta	73	181.4	180.89
Ge	32	72.60	72.65	W	74	1840	183.96
As	33	74.93	74.92	Re	75	186.31	186.22
Se	34	79.2	78.96	Os	76	190.8	190.31
Br	35	79.916	79.911	Hg	80	200.61	200.62
Kr	36	83.7	83.767	Tl	81	204.39	204.41
Rb	37	85.44	85.43	Pb	82	207.22	207.19

difficult to find an explanation, and the small outstanding difference in the case of hydrogen is a point of great interest.¹ On the whole, however, considering the fundamental differences underlying the experiments by which the figures were arrived at, the agreement is satisfactory.

116. 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

¹ V. p. 101,

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 brought us face to face with two possible alternatives. The first was to call each isotope, as it was discovered, a new element. This had serious objections. A new word would 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 had meant in all the chemical and physical literature of the past century. It would moreover be still subject to alterations in the future. The second was 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.

The second alternative has now been generally adopted. 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.

117. The Evolution of the Elements.—This subject has been the source of much interesting speculation in the past. The general opinion in the nineteenth century favoured a progress from simple to complex as is well illustrated by the following remarks of Crookes : ¹

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

¹ Crookes, Brit. Assoc. address, 1886.

When radioactivity was discovered there was naturally a change of view, for now that it was possible to observe the process of evolution actually taking place it was found that it always went the other way, heavy atoms disintegrating to form lighter ones and producing in the process helium, one of the lightest elements known. As a result theories were put forward¹ that all the elements occurring in Nature are the result of known and hypothetical radioactive disintegrations of the ordinary type, but continued far beyond the ordinary limit observed at present. For instance, if we continue the alpha ray changes of the thorium series far enough we shall ultimately reach helium.

It has been suggested by Jeans that the stars may contain elements of far higher atomic weight than any known on earth and that these in breaking down produce ordinary matter and at the same time by partial annihilation maintain the energy of the stars, but there is admittedly no experimental evidence for this.

Millikan² has put forward the idea, based upon his observations on cosmic rays, that atoms of such elements as silicon and iron are being formed continually by the aggregation of their component particles when these encounter each other in interstellar space, but the obvious improbability of such chance occurrences is a serious difficulty.

It seems most probable that in a normal hot star processes of synthesis and disintegration are occurring simultaneously and that the relatively fixed composition of a cooled fragment like the earth represents the equilibrium reached among the nuclei in process of formation and destruction at the time when rapid cooling inhibited all processes of change except the minute residual represented by radioactivity.

A most complete synthesis theory of stellar energy and of the origin of the elements founded upon modern astrophysical data has been published by Atkinson³ to which the reader is referred for further information on this interesting subject.

¹ V. p. 176.

²

V. p. 168.

³ Atkinson, *Astrophysical Jour.*, 73, 250, 1931.

CHAPTER XV

ISOTOPE EFFECT IN MOLECULAR SPECTRA

As has already been described,¹ the early optical experiments showed no detectable spectral differences in such isotopes as thorium and ionium. Later work with higher accuracy showed small differences in the line spectra² and much larger ones in the band spectra of isotopes. The theory of the "isotope effects" has now been so completely developed by means of quantum mechanics that observation of optical spectra has become a valuable addition to that of mass-spectra in the investigation of the isotopic constitution of elements. By its means exceedingly important discoveries of rare isotopes have been made and it can also be used to measure relative masses and abundances.

The isotope effect is far more clearly marked in molecular spectra than in atomic, as well as being much simpler in principle. Accordingly it seems preferable to deal first with the results from the analysis of molecular bands of diatomic molecules.

118. The vibrational effect.—The nuclei of any diatomic molecule can vibrate along the inter-nuclear axis. When the two nuclei are different, as for example in HCl or CO , the vibrations will cause a change of electric moment of the molecule, which will show itself spectroscopically in *vibrational bands* (molecules such as H_2 or N_2 , which are completely symmetrical and without any electric moment either at rest or when vibrating, obviously cannot have vibrational bands). The molecule can also rotate about a line perpendicular to the inter-nuclear axis; the quantum corresponding to this movement will be very much smaller than the vibrational quantum, and so every change in vibration will be accompanied by a number of changes in rotation. Thus if we write

$$E_{\text{vib} \cdot \text{rot}} = E_{\text{vib}}(v) + E_{\text{rot}}(J)$$

for the energy of a vibrating-rotating diatomic molecule, there will be many possible changes in J (the rotational quantum number) for one change in v (the vibrational quantum number). This is, of course, the explanation of the well-known rotational structure of

¹ V. p. 9.

² Aronberg, *Proc. Nat. Acad. Sci.*, 3, 710, 1917; Merton, *Proc. Roy. Soc.*, 96A, 388, 1920.

vibrational bands. For instance, we may take the normal case of absorption, in which the molecule in the lower state has no vibrational quanta ($v'' = 0$: we neglect half-quantum numbers for the moment) and is raised to an upper state¹ where $v' = 1$. During this transition the various J'' 's associated with $v'' = 0$ (for the molecule will be rotating, though not vibrating, in the ground state) will change both positively and negatively. Some of the J'' 's will gain in quantum number and some lose. In this way we arrive at the typical vibration-rotation band, in which for a single change in vibration such as ($v'' = 0 \rightarrow v' = 1$) we have a number of rotational lines corresponding to an increase of J ($J'' < J'$) which form an approximately evenly spaced sequence of lines, the so-called R branch, and a similar number of lines in which $J'' > J'$, the so-called P branch. The arrangement is illustrated in Fig. 37.

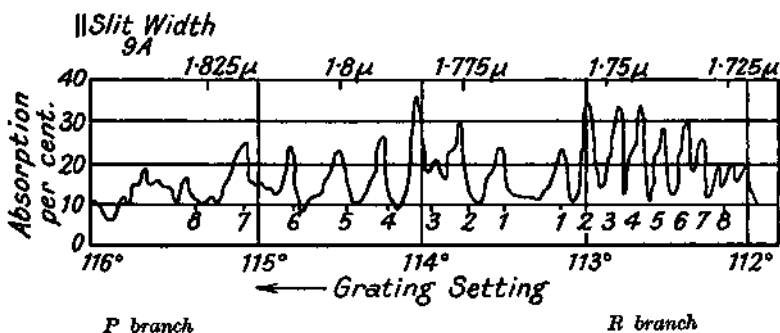


FIG. 37.—(2,0) Band of HCl under fairly low dispersion. The isotope effect is indicated, but the component lines are not resolved.

If we now consider the energy of vibration only, the way in which an isotope effect will appear in the band spectrum is very easy to see. The energy of vibration will be expressed in the usual way as

$$E_{\text{vib}/h\nu} = E(v) = w_e(v + \frac{1}{2}) - x_e w_e(v + \frac{1}{2})^2 + \dots \quad (1)$$

The vibrational quantum number v takes the values 0, 1, 2, 3 . . . , w_e is the frequency of vibrations of very small amplitude and x_e are small constants which describe the anharmonic nature of the vibrations of the nuclei.

Changes from $E''(v)$ to $E'(v)$ are permitted in which v' and v'' have any value. It is clear that a change from $v'' = 0$ $v' = 1$ will give a frequency very close to w_e , since neglecting x_e . . .

$$E(v') - E(v'') = w_e [(v' + \frac{1}{2}) - (v'' + \frac{1}{2})] \dots \quad (2)$$

¹ In conformity with the established practice, the *upper* state in an energy transition, whether of emission or absorption, is denoted by single point ('), and the *lower* state by double point ('').

Thus the position of the observed vibrational band will give a close correspondence to the actual frequency of the nuclear vibration. The order of magnitude of the nuclear vibration shows at once that the vibrational bands ($v'' = 0 \rightarrow v' = 1$) will be found between 1000 and 4000 cm^{-1} for light molecules; this range is in the near infra-red, where all vibrational-rotational bands are actually observed.

The value of w_e , the frequency of vibration of the nuclei, depends on their *reduced mass* JLL , given by $m_1 m_2 / m_1 + m_2$ where m_1 and m_2 are the nuclear masses, and the force between them. From the simplest of considerations, we can assert that for given forces

$$w_e \propto \mu^{-\frac{1}{2}}.$$

The vibrational isotope effect is at once obvious. For, assuming what is theoretically reasonable and experimentally completely proved, that the force fields in two isotopic molecules such as HC1^{35} and HC1^{37} are identical, we have

$$\frac{w_{eI}}{w_{eII}} = \frac{\mu_I^{-\frac{1}{2}}}{\mu_{II}^{-\frac{1}{2}}}.$$

From (i) and (ii) the value of w_e determines the position of the vibrational bands: and if v_{eI} is the wave number of the vibrational band of the molecular isotope I, which vibrates with a frequency of w_{eI} , then the corresponding band for the molecular isotope II, which vibrates with a frequency of w_{eU} , will be displaced by an amount which can be calculated from

$$\frac{v_{eI}}{v_{eII}} = \frac{\mu_I^{-\frac{1}{2}}}{\mu_{II}^{-\frac{1}{2}}}.$$

The quantity $\frac{\mu_I^{-\frac{1}{2}}}{\mu_{II}^{-\frac{1}{2}}}$ is usually called p .

We should expect that the molecule HC1^{37} , vibrating by reason of its increased mass a little slower than HC1^{35} , would have its vibrational band displaced towards smaller frequencies. The displacement can be calculated from the p for the two molecules and the position of the vibrational band of HC1^{35} ; it comes out as approximately 2 cm^{-1} .

This *vibrational isotope effect* clearly applies equally to all the rotational lines of a vibration-rotation band; in the vibrational spectra of HC1 these considerations predict that on the low frequency side of each rotational line of HC1^{35} there should be a less intense satellite due to HC1^{37} , about 2 cm^{-1} away. Experiment shows at once that the vibrational isotope exists in the way sketched out. In 1919 Imes^x resolved the HC1 vibration-rotation bands corresponding to

¹ Imes, *Astrophys. Jour.*, 50, 251, 1919.

vibrational changes from $0 \rightarrow 1$ and $0 \rightarrow 2$. This investigation marks the beginning of the detailed study of vibrational-rotational spectra; and the credit for it rests largely with the school at Michigan which has since carried the subject a long way towards completeness. In the (2,0) band^x he commented on the experimental fact that the rotational components were broadened on the side of small frequencies (see Fig. 37. The dispersion used by Imes was comparatively low, and lines separated by 4 cm^{-1} or so could not be sharply resolved). The explanation of this effect was given independently by Loomis² and Kratzer³ in 1920; they interpreted it as the vibrational isotope effect which has just been described. The approximate separation of the $\text{HC}1^{35}$ and $\text{HC}1^{37}$ components was taken as 4.5 cm^{-1} , in good agreement with $(p - l)\nu_e$ for the (2,0) band of $\text{HC}1$.

The general outline of the explanation was obviously sound. In fact, most of the important results derived from the isotope effect

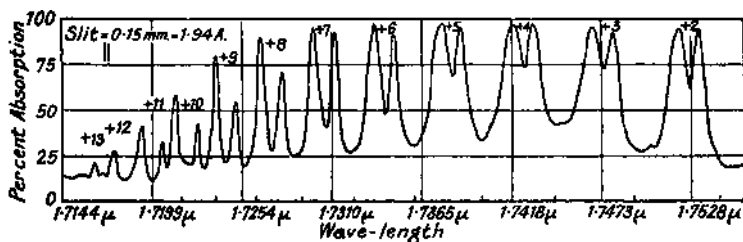


FIG. 38.—The R branch of the (2, 0) band of $\text{HC}1$ under highest dispersion yet reached in the infra-red.

The isotope components are resolved; there is no sign of $\text{HC}1^{39}$ (Hardy and Sutherland). Cf. Fig. 37. It should be noted that the direction of increasing wave-length is different in the two diagrams.

in molecular spectra are due to the simple principle of the alteration in frequency produced by an isotopic difference in p . [It should be emphasized that this effect is purely *vibrational*; each rotational line in the vibration-rotation band consists of a term $\nu_e + \nu_r$ and we are here considering only the displacement of ν_e .]

Since Imes's work the department at Michigan has made immense improvements in experimental technique in the infra-red. It is now possible to resolve completely the isotopic components of the (2,0) band of $\text{HC}1$ and measure their positions with great accuracy. The most recent and precise research, which must be something like the ultimate expression of the experimental facts, has been carried out

¹ Throughout these chapters the nomenclature suggested and adopted by Mulliken is used, (2,0) means

ν' upper state = 2; ν'' lower state = 0.

² Loomis, *Astrophys. J.*, 52, 248, 1920.

³ Kratzer, *Zeita. f. Phys.*, 3, 460, 1920.

by Hardy and Sutherland,¹ using Hardy's² infra-red spectrometer, the best of its kind so far built. Fig. 38 shows how clear-cut their results are. The lines of the HCl^{35} and HCl^{37} molecules are widely separated (compare Fig. 37) and the difference between them—the $(p - l)v_e$ —can be accurately measured. The isotopic differences for lines of the R branch are as follows :

TABLE III

ISOTOPE SEPARATIONS IN (2,0) BAND OF HCl —POSITIVE BRANCH

J (number of line)	Separation in cm^{-1}
2	404
3	403
4	403
5	4.21
6	4.21
7	414
8	4.24

From the theory of the vibrational isotope effect the differences should be exactly the same (as each line in the HCl^{37} band corresponds to the *same* vibration (0 2) and will have the same $(p - l)v_e$). They are very nearly the same ; and the vibrational effect is obviously the chief source of the displacement. But the accuracy of the experimental method is enough to give significance to the gradual increase from 404 to 4.24 with increasing values of J. This secondary effect is quite distinct from the vibrational displacement, and to understand it we must look a little more closely into the energy states of a vibrating-rotating molecule.

119. The rotational isotope effect.—The energy of a vibrating-rotating molecule can be represented approximately by

$$E(v) + E(r) = \omega_e(v + \tfrac{1}{2}) + x_e\omega_e(v + \tfrac{1}{2})^2 \dots + \frac{\hbar J}{8\pi^2 I} \cdot (J + 1) + XJ^2(J^2 + 1) \dots \quad (3)$$

where I is the moment of inertia and is expressed by μr_0 , r_0 being the distance between the nuclei at rest. $X \dots$ are small constants involving I . Each side of the equation has been divided by h .

The isotopic alteration due to the vibrational terms $\omega_e(v + \tfrac{1}{2})$, $x_e\omega_e(v + \tfrac{1}{2})^2 \dots$ has already been discussed ; the rotational terms

$\frac{\hbar J}{8\pi^2 I} (J + 1)$, $XJ^2(J + 1) \dots$ have, however, been omitted up to

now.

¹ Hardy and Sutherland, *Phys. Rev.*, 41, 471, 1932.

² Hardy, *Phys. Rev.*, 38, 2162, 1931.

$$\begin{aligned}\text{when} \quad K &= \frac{h}{4\pi^2\omega_e I}, \\ P &= \frac{3}{2}K^2(1 + 2Q_3), \\ Q &= 3 + 15Q_3 + \left(\frac{15}{2}\right)Q_3^2 + 3Q_4.\end{aligned}$$

Q_3 and Q_4 are constants in the potential energy expressions which measure the anharmonicity of the vibration.

From this we get an expression for the frequencies in any vibration-rotation bands corresponding to a change in v of ν

$$\begin{aligned}\nu &= \omega_e \Delta v + \frac{1}{2}\omega_e P \Delta v - \frac{h}{8\pi^2 I} Q (\Delta v^2 + \Delta v) \\ &\quad - J \left(-\omega_e P - \omega_e P \Delta v + \frac{h}{4\pi^2 I} - \frac{hK^2}{8\pi^2 I} \right) \\ &\quad - J^2 \omega_e P \Delta v - J^2 \left(\frac{h}{8\pi^2 I} \right) 4K^2.\end{aligned}$$

In this formula J positive gives the lines of the R branch, J negative the P branch. Terms in $\frac{h^2 K^2}{8\pi^2 I}$ have been shown by Colby¹ to be negligible.

The difference between the frequencies of molecular isotopes will be (the vibrational and rotational terms both enter, of course, into this expression)

$$\begin{aligned}\nu_I - \nu_{II} &= 1 - \rho \left[(\omega_e \Delta v - \frac{1}{2}\omega_e P \Delta v (1 + \rho + \rho^2) - \frac{hQ(\Delta v^2 + \Delta v)}{8\pi^2 I} \right] \\ &\quad + J(-\omega_e P(1 + \Delta v)(1 + \rho + \rho^2) + \frac{h}{4\pi^2 I}(1 + \rho) \\ &\quad - J^2 \omega_e P \Delta v (1 + \rho + \rho^2))\end{aligned}$$

Putting $\rho = 1$ except in the first factor

$$\begin{aligned}\nu_I - \nu_{II} &\approx 1 - \rho \left[\nu_c - \frac{h}{8\pi^2 I} Q (\Delta v^2 + \Delta v) - \frac{1}{2}\omega_e P \Delta v \right] \\ &\quad + J \left[\frac{h}{4\pi^2 I} - 3P\omega_e(1 + \Delta v) \right] - 3J^2 P \omega_e \Delta v\end{aligned}$$

$$\text{when } \nu_c = \omega_e \Delta v - \frac{1}{2}\omega_e P \Delta v - \frac{h}{8\pi^2 I} Q (\Delta v^2 + v)$$

and ν_c is the wave number of the centre of the band.

The agreement of the accurate theory with the most precise

¹ Colby, *Phys. Rev.*, 34, 53, 1929.

measurements in vibration-rotation bands is shown in Table IV, and in Table III which gives the data of Hardy and Sutherland.

TABLE IV
ISOTOPE SEPARATIONS IN THE HARMONIC BAND—POSITIVE BRANCH

3	Calculated.		Observed.				
	(cm ⁻¹).	(A).	Hardy and Sutherland.		Hettner and Bohme. ¹		Meyer and Levin. ²
			(cm ⁻¹).	(A).	(A).	(A).	
2	408	12.5	404	12.3	12.5	12.5	4.20
3	410	12.5	403	12.2	12.0	12.5	3.87
4	412	12.5	403	12.2	12.5	12.5	4.03
5	414	12.5	4.21	12.7	12.0	12.0	4.19
6	415	12.5	4.21	12.7	12.0		4.22
7	416	12.45	4.14	12.4	12.0		4.14
8	417	12.4	4.24	12.7			4.26
Mean .	413	12.5	412	12.5	12.3		413

In both cases the discrepancies are within experimental error.

121. Occurrence of the isotope effects in vibration-rotation bands of diatomic molecules.—HCl is the only diatomic molecule whose vibration-rotation bands show the isotope effects. In the other possible cases, HBr, NO, CO, the separations are smaller than the limits of experimental refinement. Our present knowledge of isotope effects would probably not have been so precise if results from electronic bands had not been brought to bear upon the observations upon vibration-rotation bands; but the intensive researches upon the (1,0) and (2,0) bands of HCl did in fact give the first proof of the phenomena and have provided the clearest illustration for those who are embarrassed by the complications of electronic bands.

122. Applications of the isotope effect in vibration-rotation bands.—As soon as the isotope effect was established, it became available as a method which has found various applications in the study of electronic bands.³ In vibration-rotation spectra, the opportunities are more limited, since the only molecule open to investigation is HCl. Even in this limited field, however, the isotope effect has had two considerable achievements.

¹ Hettner and Bohme, *Zeits. f. Physik.*, 72, 95, 1931.

² Meyer and Levin, *Phys. Rev.*, 34, 44, 1929.

³ V. p. 206.

(i) *Confirmation of the existence of H^2 .*—When Urey, Brickwedde and Murphy¹ reported the existence of H^2 (see Chapter X), it was immediately possible to confirm or deny their conclusions by work on molecular isotopes. For if H^2 existed in the quantities suggested, there would be an appreciable number of H^2C1 molecules in any volume of $HC1$, and it was clear that without using tremendous path-lengths of gas it should be possible to find the vibration-rotation bands of H^2C1 . p for H^2C1 and H^1C1 is very large, and so the vibrational separation must be great (the position of the centre of the (1,0) band is 3.46μ for $IPC1$ and so can be calculated as about 4.8μ for H^2C1); all difficulties of resolving the isotope components are removed.

Hardy, Barker and Dennison,² using a cell 7 metres long, found

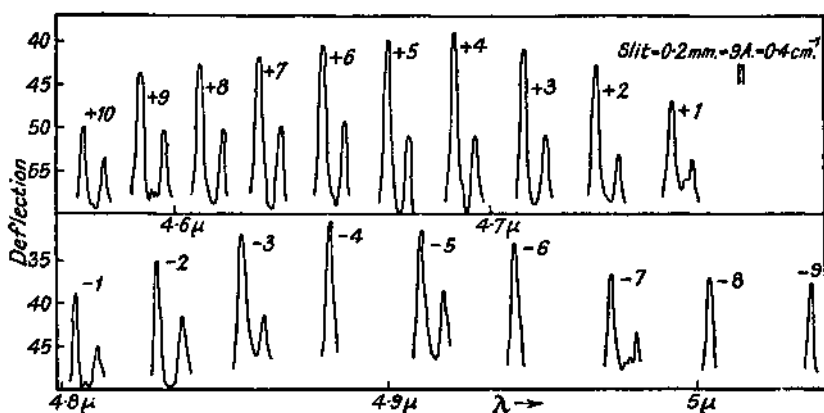


FIG. 39.—(1,0) band of H^2C1 . H^2C1^{35} and H^2C1^{87} lines are clearly visible (Hardy, Barker and Dennison).

absorption in the calculated region. The structure of the band and the agreement with theoretical prediction left no doubt that the band was the (1,0) vibration-rotation band of H^2C1^{35} . Most of the lines in the band were accompanied by weak satellites due to H^2C1^{37} (Fig. 39).

Using the measurements of Meyer and Levin upon H^1Cl , and an application of Fues's theory similar to that already described, Hardy, Barker and Dennison were able to construct an equation for their lines of H^2C1 . They made the assumption that the dimensions and force fields of the molecules of H^1Cl and H^2C1 are identical; since the only difference in the force fields in the molecules is that caused by a change in nuclear spin, this assumption must be true down to the

¹ Urey, Brickwedde and Murphy, *Phys. Rev.*, 40, 1, 1932.

² Hardy, Barker and Dennison, *Phys. Rev.*, 42, 279, 1932.

limits of hyperfine structure. This equation was then compared with the observed frequencies and p adjusted to give the best fit.

Thus from Fues's theory and Meyer and Levin's measurements the equations for the lines of H^2Cl in the (1,0) band may be written

$$\nu = (2989.24p^{1/2} - 103.40p - 0.076^{2/3}) \\ + (21.1678p - 0.6060p^{2/3} - 0.005p^2)J - 0.3030p^{2/3}J^2 - 0.3020p^2J^3.$$

In order that this equation shall fit the observed lines, the value of p has to be 0.514430, which gives a final equation

$$\nu = 2090.78 + 10.666J - 0.118J^2 - 0.00056J^3$$

The agreement between the values for the lines computed from this equation and those actually observed is very close, and the degree of error fixes the limit of accuracy of p , which is 0.514430 ± 0.000004 .

From p the mass of H^2 can be calculated. The final values arrived at, after certain assumption and corrections for which Hardy, Barker and Dennison's original paper should be read, is

$$\text{H}^2 = 201367 \pm 0.00010 \text{ (relative to } \text{H}^1 = 100778).$$

These agree satisfactorily with Bainbridge's^x results from the mass-spectrograph.²

$$\text{H}^2 = 2.01353 \pm 0.00006$$

(ii) *Disproof of existence of Cl^{39} .*—An isotope of chlorine, Cl^{39} , was considered possible at one time, but its existence was doubtful. It was thus of particular interest when, from a study of Meyer and Levin's curves for HCl , and from his own experimental work, Becker³ concluded that the spectrum showed the presence of HCl^{39} ; and this was apparently confirmed later on by Hettner and Bohme,⁴ working on the (2,0) band.

On the other hand, the spectroscopic evidence was still not satisfactory, and Hardy and Sutherland,⁵ using an apparatus of much greater sensitivity than any other employed on the problem, made a very careful re-examination of the 2,0 band. Their results are unequivocal. The previous spectroscopic data must be regarded as untrustworthy; in conditions far more favourable for the detection of the effect due to Cl^{39} , Hardy and Sutherland found no trace of it. If Cl^{39} were present in a ratio relative to Cl^{35} of 1 to 1600, they would have found it. As it is, there is not the slightest spectroscopic evidence for the existence of Cl^{39} ; and very definite spectroscopic evidence that its abundance cannot be greater than this ratio [$\text{Cl}^{39}:\text{Cl}^{35}$, 1:1600].

¹Bainbridge, *Phys. Rev.*, 41, 115, 1932; 42, 1, 1932. ² V. p. 102.

³Becker, *Zeits. f. Phys.*, 59, 583 and 601, 1930. ⁴ loc. cit.

⁵*Ibid.*

These two investigations upon the isotope effect in vibration-rotation spectra illustrate the applications which have been made more frequently of electronic band spectra :

- (i) problems of existence of isotopes (with positive results for H^2 , negative for Cl^{39}) ;
- (ii) problems of actual mass of isotopes (H^2).

123. Isotope effect in vibration-rotation spectra of polyatomic molecules.—So far no isotope effect has been definitely assigned in these spectra, very largely because the complete theoretical analysis of the structure of the bands has only recently been made. In the bands of CH_3Cl one would expect isotope effects to be observed, with the dispersion now available in the infra-red. The theory of isotope effects in polyatomic molecules has not yet been worked out, but a start is being made.¹

124. Isotope effect in electronic band spectra of diatomic molecules.²—The total energy of a molecule can be written

$$E_e + E_v + E_r$$

where E_v , E_r represent the vibrational and rotational energies in the way already described, and E_e is the electronic energy, which of course is of a greater order of magnitude than E_v or E_r . ($E_e \gg E_v \gg E_r$). Transitions between two energy states, both involving E_e , E_v , E_r , for which

$$h\nu = (E_e' + E_v' + E_r') - (E_e'' + E_v'' + E_r''),$$

are those which give rise to the *electronic band spectra* of molecules, in which a single change in E_e ($E_e' - E_e''$) is accompanied by a variety of changes in E_v (according to the many possible values of $v' - v''$) each of which vibrational transitions in turn is accompanied by a variety of rotational changes $J' - J''$. Just as there are three sources of the transitions which give the whole band structure, there will be three different possible manifestations of the isotope effect.

(i) *The electronic isotope effect.*

The electronic transition $E_e' - E_e''$ will be slightly different for different masses of one or both of the nuclei. The theory of this effect has not been worked out for even the simplest of diatomic molecules. It is, however, obvious that the effect must be very

¹ Salant and Rosenthal, *Phys. Rev.*, 42, 812, 1932.

² In this part of the chapter particularly, and also in many other ways, the writer is greatly indebted to Dr. Jevons's *Report on Band Spectra of Diatomic Molecules*. The isotope section of this book, to which reference should be made, is up to the very high level of clarity and comprehensiveness which distinguishes the whole work.

small; in practice, it has proved to be outside the range of experimental observation. Presumably, in the band spectra of isotopic molecules each line has a sort of isotopic hyperfine structure of separations less than 01 cm^{-1} . For all present purposes, this can be completely ignored.

(ii) *The vibrational isotope effect.*

(iii) *The rotational isotope effect.*

These will apply in precisely the manner developed for vibration-rotation spectra. And so, since the electronic effect is negligible, the total isotope effect in electronic band spectra will be the algebraic sum of the vibration and rotation isotopic effects, exactly as in the vibration-rotation bands of HCl.

The vibrational isotopic effect, which is much larger,¹ has been much the more important in the history of band spectra. The form

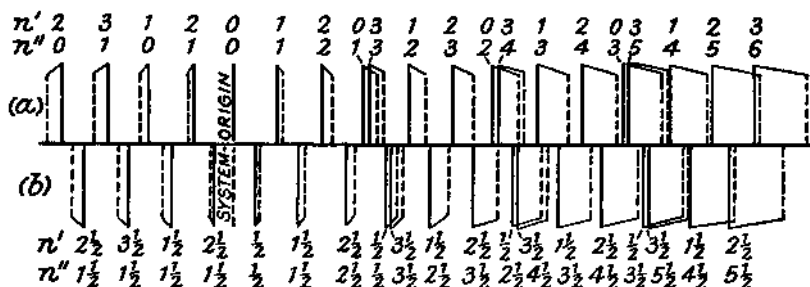


FIG. 40.—Typical Pattern of Vibrational Isotope Effect in Electronic Bands. (After Mulliken.)

it takes in electronic bands follows at once from the equation (3),² from which it is clear that the vibrational isotope effect is constant for the lines of a given band (given values of v' , v'' and v), and that the isotopic displacement increases linearly from band to band with the interval v_v .

A diagram reproduced from one of Mulliken's early papers shows these results (Fig. 40). The case illustrated is that when the heavier molecule is the more abundant, as in $\text{B}^{11}\text{O}^{16}$, $\text{B}^{10}\text{O}^{16}$ and $p - 1$ is negative: the band sequences are overlapping. The comparison between (a) and (b) was designed to show the difference between the effect for whole and half quantum numbers.

The magnitude of the vibrational isotopic displacement varies with the atomic weights, with $p - 1$, which itself is approximately proportional to $M - M^1$ (when M , M^1 are the masses of the atomic isotopes in the molecules).

¹ V. p. 198.

² V. p. 197.

Another of Mulliken's diagrams illustrates this effect of mass (Fig. 41).

The rotational isotope effect was shown to depend on $p^2 - 1$.

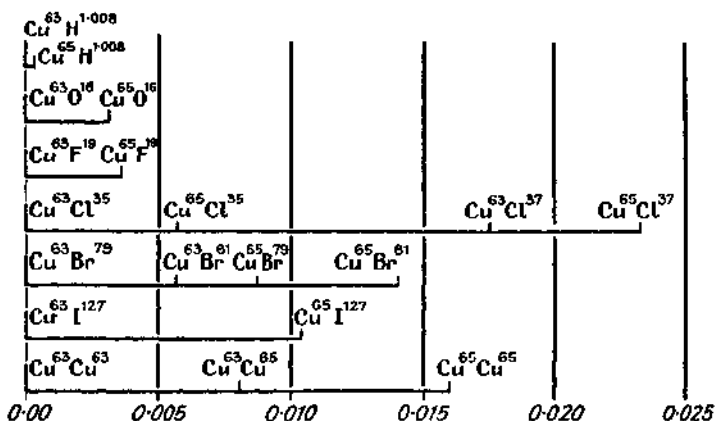


FIG. 41.—Calculated Values of $p - 1$ for Copper Compounds. (From Mulliken.)

The variation of the effect with J , the rotational quantum number, is demonstrated in Fig. 42. The full curves represent the hypothetical

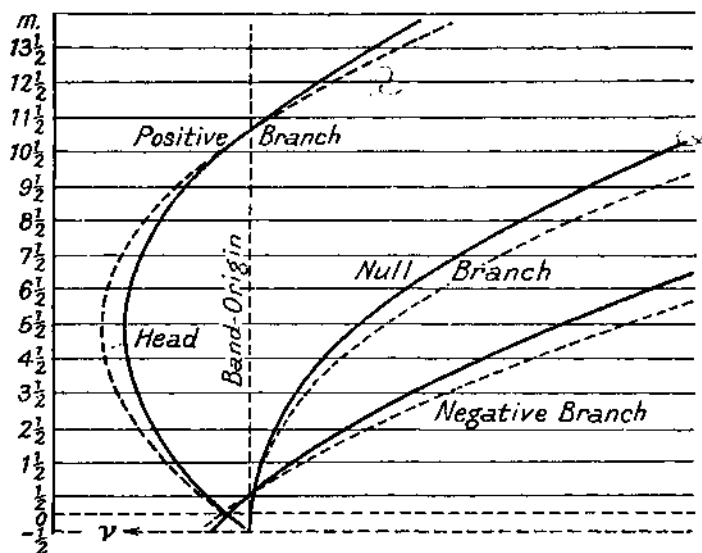


FIG. 42.—Rotational Isotope Effect in Electronic Bands, shown as a Fortrat Diagram.

bands for the more abundant of two isotopic molecules; for each value of J , the less abundant molecule has a different rotational shift illustrated by the dotted curves.

Since ν_r is so much smaller than ν_e , the rotational isotope effect is smaller than the vibrational: and it is usual to determine p from a study of the vibrational effect alone, by measuring the displacements of lines of small J , for which the rotational shift is negligible.

125* Applications of the isotope effect in electronic bands of diatomic molecules.—As in the example of H^2 already discussed under vibration-rotation spectra, there is one application of the isotope effect which is of great general interest. Several rare isotopes have been discovered from the isotope effect in band spectra. In fact the unequivocal identification of a number of isotopes has been the chief spectroscopic contribution to the subject.

(i) *Discovery of new isotopes.*

The procedure described for H^2Cl is quite representative of the search for isotopes in electronic band spectra. Sometimes, of course, the discovery of an isotopic spectrum has been a matter of chance; instead of going out to look in a calculated position for a spectrum of given structure, workers have found satellite bands which later were proved to be isotopic components. However, after the initial recognition of the bands, the method of Hardy, Barker and Dennison is substantially that used for the discovery of isotopes since Mulliken¹ proved the existence of Si^{30} . In all cases, the construction of an equation derived from the principal band and involving p , the proof or disproof that this equation can account for the observed lines, and the evaluation of p , are standard operations.

Some of the most interesting of recent results are those on the isotopes of oxygen, nitrogen, carbon and beryllium. For fuller details, reference should again be made to Jevons's monograph, but a brief description is desirable here.

Oxygen.—Close to the well-known red atmospheric bands of O_2 ($^3\Sigma$ $^1\Sigma$) Dieke and Babcock² observed a weaker band of very much the same structure. Giauque and Johnston³ showed that these lines could be interpreted as due to $O^{18}O^{16}$, the calculated isotopic shifts agreeing extremely well with the observed separations. There are also twice as many rotational lines in the $O^{18}O^{16}$ band as in the $O^{16}O^{16}$ band, as required by the theory of symmetrical and anti-symmetrical terms.

Babcock⁴ showed also that another system of weak lines near to the main band could be explained as due to $O^{17}O^{16}$.

¹ Mulliken, *Phys. Rev.*, 26, 319, 1925.

² Dieke and Babcock, *P.N.A.S.*, 13, 670, 1927.

³ Giauque and Johnston, *Nature*, 123, 318 and 831, 1929.

⁴ Babcock, *Nature*, 123, 761, 1929.

From the values of p , obtained in a similar way to that described for H^2Cl , the mass of O^{18} is calculated to be 180065 on the basis of $\text{O}^{16} = 16$; the mass of O^{17} is 170029.

After these results upon the O_a bands had been reported, Naude¹ made a search of the $^2\Sigma - ^2\Pi$ system of NO , and found bands due to $\text{N}^{14}\text{O}^{17}$ and $\text{N}^{14}\text{O}^{18}$.

Nitrogen.—As well as finding the bands of oxygen isotopes in NO , Naude also discovered the bands of $\text{N}^{15}\text{O}^{16}$ in the same system. This was confirmed by Herzberg² from a study of the $^3\Pi - ^3\Pi$ bands of N_2 .

Carbon.—In a study of the Swan bands, King and Birge³ discovered bands which they proved due to $\text{C}^{13}\text{C}^{12}$. [Plate VIII gives a very beautiful illustration of part of the main $\text{C}^{12}\text{C}^{12}$ band and the isotopic component.] The value of p gives a mass of $\text{C}^{13} = 13$ very nearly (on the basis of $\text{C}^{12} = 12$).

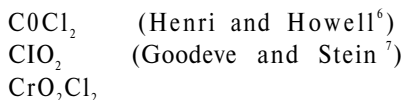
The isotope C^{13} was also proved present in the fourth positive bands of CO and the violet bands of CN .

Beryllium.—Watson⁴ has suggested that lines due to Be^8H occur in the $^2\Sigma - ^2\Sigma$ system of BeH . The case put forward, though ingenious and suggestive, has to introduce more assumptions than are necessary in the other examples: and further experimental work by Olsson⁵ indicates that Be^8H lines are not present. The spectroscopic evidence for Be^8 cannot be taken as definite.

(ii) *Other applications of the isotope effect.*

The isotope effect has some important applications in technical spectroscopy, for instance in identifying the molecule responsible for a band system and in assigning (ν' , ν'') values to bands in a system. Jevons's monograph includes a clear exposition of these methods.

126. The isotopic effect in the electronic band spectra of polyatomic molecules.—Henri first showed an indubitable isotope effect in the band spectrum of COCl_2 . Since then, the phenomenon has been observed in the bands of several molecules containing chlorine, e.g.



¹ Naudé, *Phys. Rev.*, 36, 333, 1930.

² Herzberg, *Zeits. f. Phys. Chem.*, 9B, 43, 1930.

³ King and Birge, *Nature*, 124, 127, 1929, and *Astrophys. J.*, 72, 19, 1930.

⁴ Watson and Parker, *Phys. Rev.*, 36, 1019, 1930.

⁵ Olsson, *Zeits. f. Phys.*, 73, 732, 1932.

⁶ Henri and Howell, *Proc. Roy. Soc.*, 128, 178, 1930.

⁷ Goodeve and Stein, *Trans. Farad. Soc.*, 738, 1929.

Fig. 43, showing part of a band in CrO_2Cl_2 , illustrates the appearance of the effect. The theory seems to be rather complicated: for each of the possible nuclear vibrations the isotope effect may be different, and will only be the same for reasons of symmetry: obviously in a molecule like ClX_2 , in which the nuclei are considered to be in a straight

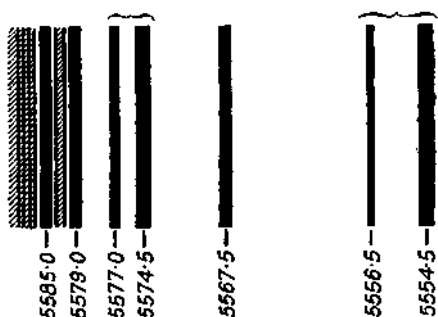


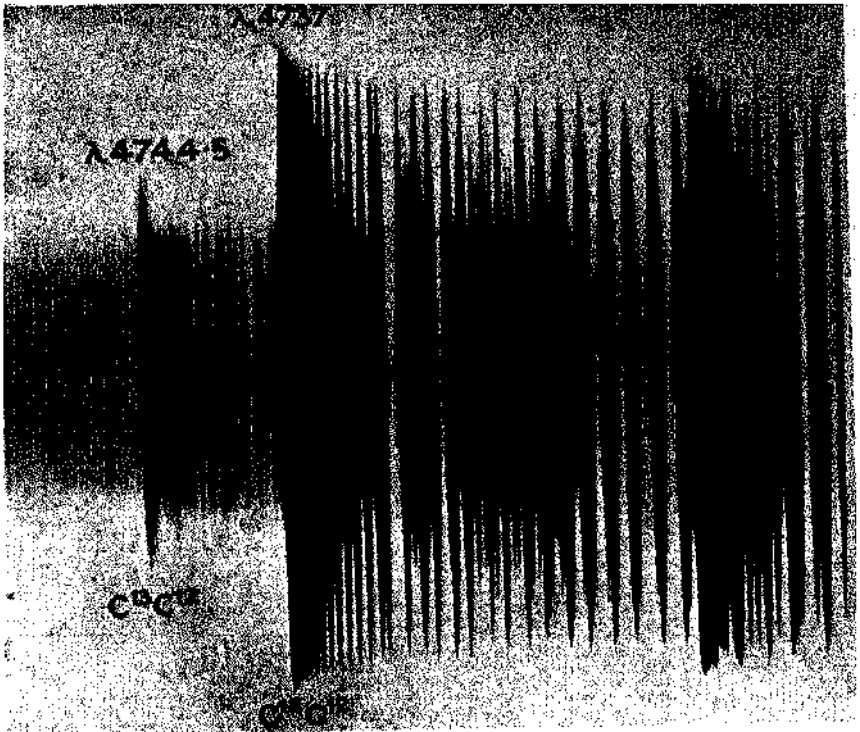
Fig. 43.—Isotope Effect in a Polyatomic Molecule.

Sketch of a typical arrangement of lines in the electronic bands of CrO_2Cl_2 (as studied by C.P.S.). Note the isotope pairs (5577, 5574.5) and (5556.5, 5554.5).

line, the symmetrical vibration of the X's along the axis $\text{X} \quad \text{Cl} \quad \text{X}$ will give no isotope effect at all, and the vibrations $\text{X} - \text{Cl} - \text{X}$ and $\text{X} \quad \text{Cl} \quad \text{X}$ will give different isotope effects. So far, however, the quantitative theory is only just being developed: ¹ it ought soon, however, to be possible to use the effects as a valuable qualitative criterion in the assignment of types of vibration.

In Table V are summarized the principal results so far obtained from the investigation of the isotope effect in band spectra.

¹ Salant and Rosenthal, loc. cit.



ISOTOPE EFFECT IN OPTICAL SPECTRA
 Upper: Band Spectra of Carbon.
 Lower: $H\alpha$ - and $H\beta$ -Lines of Hydrogen.

TABLE V

A SUMMARY OF OBSERVATIONS OF THE ISOTOPE EFFECT IN DIATOMIC SPECTRA

Element.	Atomic Num-ber.	Atomic Weight.	Mass or Proton Numbers. M M'	Abund-ance Ratio. $\alpha : 1$	Band-Systems.	Isotopic Molecules. MM' M'M'	$\rho - 1$.
H	1	1.008	1 2		HCl infra-red	H ¹ Cl ³⁵ H ¹ Cl ³⁷ H ² Cl ³⁵ H ² Cl ³⁷	-0.51443
Li	3	6.940	7 6	10.2 : 1	LiH Li ₂ , blue-green	Li ⁷ H Li ⁷ Li ⁷ Li ⁶ H Li ⁶ Li ⁷	+ .01036 + .04083
Be	4	9.02	9 8	2000 : 1	BeH, λ 4991	Be ⁹ H Be ⁸ H	+ .00823
B	5	10.82	11 10	4.3 : 1	BH, λ 4100 BO α and β	B ¹¹ H B ¹⁰ H B ¹¹ O ¹⁶ B ¹⁰ O ¹⁶	+ .01942 + .02908
C	6	12.003	12 13	850 : 1	C ₂ , Swan CN, Violet CO, fourth posi- tive	C ¹² C ¹² C ¹² C ¹³ C ¹³ N ¹⁴ C ¹³ N ¹⁴ C ¹² O ¹⁶ C ¹³ O ¹⁶	- .01942 - .02093 - .0223
N	7	14.008	14 15	346 : 1	N ₂ , second posi- tive NO, γ	N ¹⁴ N ¹⁴ N ¹⁵ N ¹⁴ N ¹⁴ O ¹⁶ N ¹⁵ O ¹⁶	- .01681 - .01794
O	8	16.000	16 18 17	630 : 1 : $\frac{1}{2}$	NO, γ O ₂ , atmospheric	O ¹⁶ N ¹⁴ O ¹⁶ N ¹⁴ O ¹⁷ N ¹⁴ O ¹⁷ N ¹⁴ O ¹⁶ O ¹⁶ O ¹⁶ O ¹⁶ O ¹⁶ O ¹⁸ O ¹⁷ O ¹⁶	- .02627 - .01382 - .02818 - .01482
Mg	12	24.32	24 25 26	7 : 1 : 1	MgH, λ 5211 MgH ⁺	Mg ²⁴ H Mg ²⁵ H Mg ²⁴ H ⁺ Mg ²⁵ H ⁺ Mg ²⁵ H ⁺ Mg ²⁴ H ⁺	- .00080 - .00154 - .00080 - .00164
Si	14	28.06	28 29 30		SiN	Si ²⁸ N ¹⁴ Si ²⁹ N ¹⁴ Si ³⁰ N ¹⁴	- .00576 - .01117
Cl	17	35.457	35 37	3.18 : 1	HCl infra-red Cl ₂ , visible ab- sorption CaCl CuCl, four sys- tems SrCl AgCl ultraviolet absorption SnCl two ultra- violet systems ICI red absorption BaCl AuCl two systems HgCl TlCl absorption	Cl ³⁵ H Cl ³⁵ Cl ³⁵ C ³⁷ Cl ³⁵ Cl ³⁵ Ca ⁴⁰ Cl ³⁷ Ca ⁴⁰ Cl ³⁵ Cu ⁶³ Cl ³⁷ Cu ⁶³ Cl ³⁵ Cu ⁶⁵ Cl ³⁷ Cu ⁶⁵ Cl ³⁵ Sr ⁸⁶ Cl ³⁷ Sr ⁸⁶ Cl ³⁵ Sr ⁸⁸ Cl ³⁷ Sr ⁸⁸ Cl ³⁵ Ag ¹⁰⁷ Cl ³⁷ Ag ¹⁰⁷ Cl ³⁵ Ag ¹⁰⁹ Cl ³⁷ Ag ¹⁰⁹ Cl ³⁵ Sn ¹¹⁹ Cl ³⁷ Sn ¹¹⁹ Cl ³⁵ I ¹²⁷ Cl ³⁷ I ¹²⁷ Cl ³⁵ Ba ¹³⁶ Cl ³⁷ Ba ¹³⁶ Cl ³⁵ Ba ¹³⁸ Cl ³⁷ Ba ¹³⁸ Cl ³⁵ Au ¹⁹⁷ Cl ³⁷ Au ¹⁹⁷ Cl ³⁵ Hg ^{200.6} Cl ³⁷ Hg ^{200.6} Cl ³⁵ Tl ²⁰⁴ Cl ³⁷ Tl ²⁰⁴	- .00075 - .01361 - .01452 - .10753 - .01772 - .01940 - .01853 - .02058 - .02067 - .02111 - .02142 - .02173 - .02180 - .02322 - .02328 - .02334

TABLE V—(continued)

Element.	Atomic Number.	Atomic Weight.	Mass or Proton Numbers.		Abundance Ratio. $\alpha : 1$	Band-Systems.	Isotopic Molecules.		$\rho - 1$.
			M	M'			MM'	M'M	
K	19	39.10	39	41	18 : 1	K ₂ Orange-red	K ³⁹ K ³⁹	K ⁴¹ K ³⁹	-01223
Cu	29	63.57	63	65	2.5 : 1	CuH, $\lambda\lambda$ 4280, 4328	Cu ⁶³ H	Cu ⁶⁵ H	-00024
						CuF	Cu ⁶³ F ¹⁹	Cu ⁶⁵ F ¹⁹	-00357
						CuCl, four sys- tems	Cu ⁶³ Cl ³⁵	Cu ⁶⁵ Cl ³⁵	-00651
							Cu ⁶³ Cl ³⁷	Cu ⁶⁵ Cl ³⁷	-00571
						CuBr, three sys- tems	Cu ⁶³ Br ⁷⁹	Cu ⁶⁵ Br ⁷⁹	-00860
							Cu ⁶³ Br ⁸¹	Cu ⁶⁵ Br ⁸¹	-00860
Zn	30	65.38	64	66		ZnI	Zn ⁶⁴ I ¹²⁷	Zn ⁶⁶ I ¹²⁷	-01032
Ge	32	72.60	74	72 76		GeS absorption	Ge ⁷⁴ S ³²	Ge ⁷⁶ S ³²	+00859
								Ge ⁷⁴ S ³²	+00419
								Ge ⁷⁶ S ³²	-00398
Br	35	79.916	79	81	1 : 1	CuBr, three sys- tems	Br ⁷⁹ Cu ⁶³	Br ⁸¹ Cu ⁶³	-00549
						Br, visible ab- sorption	Br ⁷⁹ Cu ⁶⁵	Br ⁸¹ Cu ⁶⁵	-00559
							Br ⁷⁹ Br ⁸¹	Br ⁷⁹ Br ⁷⁹	+00623
								Br ⁸¹ Br ⁸¹	-00627
						SrBr	Br ⁷⁹ Sr ⁸⁶	Br ⁸¹ Sr ⁸⁶	-00646
							Br ⁷⁹ Sr ⁸⁸	Br ⁸¹ Sr ⁸⁸	-00653
						AgBr	Br ⁷⁹ Ag ¹⁰⁷	Br ⁸¹ Ag ¹⁰⁷	-00713
							Br ⁷⁹ Ag ¹⁰⁹	Br ⁸¹ Ag ¹⁰⁹	-00724
						BaBr	Br ⁷⁹ Ba ¹³⁶	Br ⁸¹ Ba ¹³⁶	-00784
							Br ⁷⁹ Ba ¹³⁸	Br ⁸¹ Ba ¹³⁸	-00788
						HgBr	Br ⁷⁹ Hg ²⁰²	Br ⁸¹ Hg ²⁰²	-00897
Sr	38	87.63	88	86	30 : 1	TlBr absorption	Br ⁸¹ Tl ²⁰⁴	Br ⁷⁹ Tl ²⁰⁴	+00900
						SrF yellow-green	Sr ⁸⁶ F ¹⁹	Sr ⁸⁸ F ¹⁹	+00206
						SrCl	Sr ⁸⁶ Cl ³⁵	Sr ⁸⁸ Cl ³⁵	+00330
							Sr ⁸⁶ Cl ³⁷	Sr ⁸⁸ Cl ³⁷	+00344
Ag	47	107.880	107	109	71 : 1	SrBr	Sr ⁸⁶ Br ⁷⁹	Sr ⁸⁸ Br ⁷⁹	+00549
							Sr ⁸⁶ Br ⁸¹	Sr ⁸⁸ Br ⁸¹	+00556
						AgH	Ag ¹⁰⁷ H	Ag ¹⁰⁹ H	-00001
						AgCl	Ag ¹⁰⁷ Cl ³⁵	Ag ¹⁰⁹ Cl ³⁵	-00226
Ba	56	137.36	138	136		AgCl	Ag ¹⁰⁷ Cl ³⁷	Ag ¹⁰⁹ Cl ³⁷	-00238
						AgBr	Ag ¹⁰⁷ Br ⁷⁹	Ag ¹⁰⁹ Br ⁷⁹	-00390
						AgI	Ag ¹⁰⁷ Br ⁸¹	Ag ¹⁰⁹ Br ⁸¹	-00398
							Ag ¹⁰⁷ I ¹²⁷	Ag ¹⁰⁹ I ¹²⁷	-00499
Ba	56	137.36	138	136		BaCl	Ba ¹³⁶ Cl ³⁵	Ba ¹³⁸ Cl ³⁵	+00149
							Ba ¹³⁶ Cl ³⁷	Ba ¹³⁸ Cl ³⁷	+00165
						BaBr	Ba ¹³⁶ Br ⁷⁹	Ba ¹³⁸ Br ⁷⁹	+00267
							Ba ¹³⁶ Br ⁸¹	Ba ¹³⁸ Br ⁸¹	+00272
Hg	80	200.01	202	200 204		HgH, ² H ₁ $\rightarrow$ ² Σ	Hg ²⁰² H	Hg ¹⁹⁹ H	+000050
								Hg ²⁰⁰ H	+000025
								Hg ²⁰⁴ H	-000024
Pb	82	207.22	208	206 207	7 : 4 : 3	PbO Systems A and C	Pb ²⁰² O ¹⁶	Pb ²⁰⁶ O ¹⁶	+00035
								Pb ²⁰⁷ O ¹⁶	+00017

CHAPTER XVI

THE ISOTOPE EFFECT IN ATOMIC SPECTRA

Isotope effects do not play an important part in atomic spectra. There are, however, two ways, one direct and one indirect, in which the presence of isotopes may show themselves.

127. The electronic isotope effect.—For atoms or ions which consist of a single electron revolving round a nucleus of mass M , the principal spectral lines will be given by Bohr's equation

$$\nu = \frac{2\pi^2 E^4}{ch^3} \frac{Mm_e}{M + m_e} \left(\frac{1}{n'^2} - \frac{1}{n''^2} \right) \quad . \quad . \quad . \quad (1)$$

where n' and n'' are the principal quantum numbers of the upper and lower states, and $E = e, 2e, 3e, 4e \dots$ for $H, He^+, Li^{++}, Be^{+++} \dots$

Obviously, if the nucleus exists in the isotopic masses M and M' , here will be satellite lines represented by :

$$\begin{aligned} \nu' - \nu = \frac{2\pi^2 E^4}{ch^3} \left(\frac{M' m_e}{M' + m_e} - \frac{M m_e}{M + m_e} \right) \left(\frac{1}{n'^2} - \frac{1}{n''^2} \right) \\ \div \frac{m_e(M' - M)\nu}{MM'} \quad . \quad . \quad (2) \end{aligned}$$

This relation has recently been put to a dramatic use in the discovery of H^2 . Urey, Brickwedde and Murphy¹ calculated that, if this isotope existed, there would be isotopic components of the Balmer lines shifted to the short wave-length side of $H^1\alpha, \beta, \gamma, \delta$ by 4.16, 5.61, 6.29 and 6.65 cm^{-1} respectively. The successful result of their search for these lines is beautifully illustrated by Plate VIII. In this plate $H^1\alpha$ and $H^2\alpha$, $H^1\beta$ and $H^2\beta$ all appear and are separated by exactly the calculated distance.

In itself, the appearance of a very weak line near each Balmer line would not have been quite convincing ; but Urey and his colleagues made their proof definite by preparing three samples of hydrogen in which the proportions of H^2 —if any existed—had been raised by fractional distillations and by showing that the intensities of the lines in the positions calculated for H^2 were in agreement with

¹ loc. cit.

the proportion of H^2 believed to be in the samples. Thus, on the assumption that H^2 existed, their third sample was prepared so as to be considerably richer in H^2 than the others; and this sample gave much enhanced lines at the wave-lengths calculated for H^2 . After these experiments, there was no doubt that H^2 existed.

The H^2 line has the doublet structure which, of course, was anticipated. The comparison of the positions of the lines calculated from equation (2) and actually observed, is shown in Table VI.

	Ha.	H β .	H γ .	H δ .	
Calculated displacement	1.743	1.326	1.185	1.119 cm ⁻¹	
Observed :					
Ordinary Hydrogen		1.346	1.206	1.145	
		1.230	1.191	1.103	
Samples II and III .	1.791	1.313	1.176	1.088	

A rough estimate of the proportions of H^2 in ordinary hydrogen gave a value of 1 in 4000 or less, but the figure can only be a crude approximation.

Equation (2) can only be used with accuracy in the case of hydrogen; and it ceases to apply at all when the atom has more than one electron outside the nucleus. For two-electron and three-electron atoms the theory has been worked out by Hughes and Eckart.¹ The separations of $Li^7 - Li^6$ have been measured by Hughes² and shown to be in reasonable agreement with the theoretical predictions. Hughes's observations were :

$$\begin{array}{llll}
 Li+2^3P & 1^3S: & \nu' - \nu = & 1.06 \text{ cm}^{-1} \text{ (to longer A)} \\
 Li: 2^3P & 1^3S: & \nu' - \nu = & 0.345 \text{ cm}^{-1} \\
 Li: 3^3P & 1^3S: & \nu' - \nu = & 0.56 \text{ cm}^{-1}.
 \end{array}$$

The theory of the effect for an atom with more than three electrons has not been established; and there are few observations, perhaps only those upon the lines of neon, which demonstrate the effect experimentally for such atoms. The effect will obviously be very small, and it is always likely to be confused with the hyper-fine structures.

128. The effect of the nuclear spin of isotopes.—The spectroscopic effects discussed up to now (the rotational and isotope effects in band spectra and the electronic effect in fine spectra) have been

¹ Hughes and Eckart, *Phys. Rev.*, 36, 694, 1930.

² Hughes, *Phys. Rev.*, 38, 857, 1931.

caused entirely by the differences in *mass* of the isotopic nuclei. There is one other difference in isotopic nuclei which may be revealed spectroscopically: the spin moments of isotopic nuclei may not be the same, and accordingly the features of the spectra which depend on nuclear spin may show differences for different isotopes.

At the moment, the results are rather scanty. If we could be certain of the values of the nuclear spin of certain isotopes, our views of nuclear structure might become suddenly clarified. The value of the spins of H^2 , Cl^{37} , N^{15} . . . are some of the most important unknown facts of nuclear physics.

Very probably the information will be obtained before long.¹ It seems best to describe in outline here the methods by which nuclear spins are found, to give a list of those nuclei the spins of which are known, and to show the gaps where the spins of isotopes have not yet been measured.

129. Hyper-fine structures of atomic line spectra.—Many spectral lines, particularly those of heavy atoms, show a narrow structure with separations less than 1 cm^{-1} . This "hyper-fine structure" may, and probably is, due to more than one cause; but it cannot be explained in terms of electronic states alone; whatever the cause is, it is necessary to invoke some interaction of the electrons with the *nucleus*.

It is possible that the presence of isotopic nuclei produces some of these hyper-fine structures, perhaps in the way mentioned on p. 211. On the other hand, the presence of isotopes cannot be all the truth, for hyper-fine structure is clearly marked for atoms which have no isotopes. Thus, as an explanation for the greater number, though not all, of hyper-fine structures, the idea of nuclear spin has been adopted. Pauli² first pointed out that if a mechanical moment of the nucleus were assumed, there would, of course, be an associated magnetic moment, whose interaction with the extra-nuclear electrons could be used to explain the hyper-fine splitting. The magnetic moment will probably be of the order of m/M that of the electron, which would give an observable hyper-fine separation for heavy atoms. The mechanical moment can be represented by $ih/2\pi$ where i is the nuclear spin quantum number.

The interaction of the nuclear and electronic moments, and the production of hyper-fine levels, can be illustrated in the usual imperfect but useful way by a vector model.

With i the mechanical moment of the nucleus and j the mechanical

¹ Lewis and Ashley (*Phys. Rev.*, 43, 837, 1933) have recently shown that the spin of H^2 is very probably 1.

² Pauli, *Naturwiss.*, 12, 741, 1924.

moment of the electron, the resultant of i and j will assume different values, in the normal process of addition of vectors. The resultant can be called f (the hyper-fine quantum number). The number of levels will be $2j + 1$ if $j < i$ and $2i + 1$ if $i < j$.

As an example,

$$\begin{aligned} &\text{if } i = 5/2 \\ &\text{and } j = 1/2, \end{aligned}$$

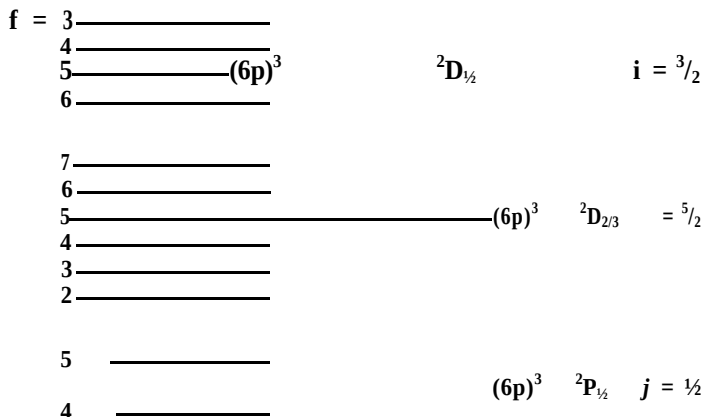
f assumes two values, 2 and 3, in the ordinary vector summation. Very much the same considerations apply as for the vector formation of j from l and s ; and so the selection rule will be $\Delta f = \pm 1, 0$, and $f = 0 \rightarrow f = 0$ is forbidden.

The separation formulae have been definitely established for configurations with a deeply penetrating s electron, but are otherwise liable to change with the production of new data, and it would be out of place to consider them here. Pauling and Goudsmit's book on *The Structure of Line Spectra* gives a very full account up to 1931, but the subject is moving very quickly and reference should be made to original papers.

However, it is possible to describe how i is obtained from measurements of hyper-fine structure in a case where there seems to be fewer complications than in most atoms—Bi.

Goudsmit and Back¹ made a very satisfying examination of the hyper-fine structure of a number of lines in the spectrum of Bi: they succeeded in assigning hyper-fine levels which explained the structure observed simply and naturally.

Thus a scheme on the following lines :



5	_____		
4	_____	$2s^1$	$j = \frac{1}{2}$
4	_____		
5	_____	$3s$	$j = \frac{1}{2}$
4	_____		
5	_____	$3d''''$	$j = \frac{1}{2}$
$f = 6$	_____		
5	_____	$4d''$	$j = \frac{3}{2}$
4	_____		
3	_____		

In each case the number of bands is $2j + 1$, in accordance with the theory : and transition between these levels, with $f = \pm 1, 0$ gives exactly the hyper-fine structure observed for $X 4722 \text{ Bi}$, ($^2D_{\frac{1}{2}} - ^2S$), etc. The six-fold structure of $n4722$, predicted by the above scheme, is actually observed.

Since for the level where $j = f$ there are $2j + 1$ hyper-fine levels, then i must be equal to or larger than $^5/2$.

In order to determine i definitely, Back measured the Zeeman effect of the hyper-fine structure. In the case where the external magnetic field is strong, the theory is simple. The interaction of i and j with the field is much greater than with one another. That is, the coupling between i and j is broken and each has its quantized projection on the external field, H . The component of i along H can be called m_i , and of J , m_j . Then the magnetic state can be written

$$W_H = \frac{eh}{4\pi m_0 c} H(m_i g(i) + m_j g)$$

where g is the Lande factor. $g(i)$ will be very small, since the factor m_c/M enters, and $m_i g(i)$ will be undetectable. So, to a first approximation, the Zeeman effect is the same with a nuclear moment as without. If, however, we include the interaction of the magnetic nucleus and the extranuclear electrons we have to write the total interaction energy as—

$$W = \frac{eh}{4\pi m_0 c} H\{m_i g(i) + m_j g\} + Aij \cos \bar{ij}$$

¹ These four levels are denoted by a non-committal notation, since they are not known unequivocally.

where $m_i g(i)$ is negligibly small and A is the separation constant. For a strong field, the second term is smaller than the first.

$ij \cos ij$ becomes $m_i m_j$, and the expression for the energy is

$$E = \frac{eh}{4\pi m_0 c} m_i g + A m_i m_j.$$

The first term is the ordinary Zeeman effect, and so with every Zeeman level there will be a hyper-fine structure determined by $A m_i m_j$; m_i can assume all the $2i + 1$ values from $-i \dots +i$. Thus every Zeeman level will be split into $2i + 1$ equidistant levels with a separation of $A m_j$; and since m_j does not change during a transition, each of the $2i + 1$ levels of the initial Zeeman state combines with only one of the $2i + 1$ levels of the upper state. Thus the Zeeman lines themselves have a very simple pattern: each Zeeman component is split into a hyper-fine structure of $2i + 1$ equidistant lines.

Accordingly if the Zeeman effect of the hyper-fine structure can be measured, the number of hyper-fine lines in each component gives an unambiguous value of i . Back resolved the hyper-fine structure of four Zeeman components of $n4722$ of Bi. Each was split into ten components and so for the bismuth nucleus $2i + 1 = 10$ and $i = 9/2$.

The greater number of nuclear spins so far known have been measured in this way, though few with such definiteness. Apart from the method of hyper-fine structure there are two other quite distinct ways of determining nuclear spins.

130. Nuclear spins from alternating intensities in molecular spectra.—The rotational levels of a completely symmetrical molecule fall into two classes, called symmetrical (s) and anti-symmetrical (a), which depend upon properties of the wave function. Transition can only take place between s and s and a and a levels. Now the statistical weight of an anti-symmetrical level J is less than the mean of the weights of the neighbouring symmetrical levels of $J + 1$ and $J - 1$, i.e. the levels have two sets of statistical weights

$$g_s(2J + 1) \text{ and } g_a(2J + 1) \text{ and } g_s > g_a$$

In this way the s and a levels can be thought of as *strong* and *weak* levels, and transitions between them will give *strong* and *weak* lines—the well-known alternating intensities in the spectrum of symmetrical molecules. An unsymmetrical molecule (such as NO and $\text{Cl}^{35}\text{Cl}^{37}$) will have rotational levels all of statistical weight $2J + 1$, and the phenomenon of alternating intensities disappears.

The occurrence of s and a levels depends upon the existence of a nuclear moment, in such a way that

$$\frac{g_s}{g_a} = \frac{i + 1}{i}$$

TABLE VII
NUCLEAR SPINS

Atomic Number.	Element.	Mass Number.	Nuclear Spin.	Method.
1	H	1	$\frac{1}{2}$	Alt. int.
2	He	4	0	Alt. int.
3	Li	6	0	Hyp. str.
	Li	7	$\frac{3}{2}$	Alt. int. Hyp. str.
6	C	12	0	Alt. int.
7	N	14	1	Alt. int.
8	O	16	0	Alt. int.
9	F	19	$\frac{1}{2}$	Alt. int.
11	Na	23	$\frac{3}{2}$ or $\frac{5}{2}$	Alt. int. and atomic rays (disagreement: $\frac{3}{2}$ prob- able)
15	P	31	$\frac{1}{2}$	Alt. int.
16	S	32	0	Alt. int.
17	Cl	35	$\frac{3}{2}$	Alt. int.
19	K	39	$> \frac{1}{2}$	Alt. int.
25	Mn	55	$\frac{5}{2}$	Hyp. str.
29	Cu	63	$\frac{3}{2}$	Hyp. str.
	Cu	65	$\frac{3}{2}$	
31	Ga	69	$\frac{3}{2}$	Hyp. str.
	Ga	71	$\frac{3}{2}$	
33	As	75	$\frac{3}{2}$	Hyp. str.
35	Br	79	$\frac{3}{2}$?	Hyp. str. and alt. int.
	Br	81	$\frac{3}{2}$?	
37	Rb	85	$\frac{3}{2}$?	Hyp. str.
48	Cd	111, 113	$\frac{1}{2}$	Hyp. str.
	Cd	110, 112, 114, 116	0	
49	In	115	$\frac{3}{2}$	Hyp. str.
51	Sb	121	$\frac{3}{2}$?	Hyp. str.
		123	$\frac{3}{2}$?	
53	I	127	$\frac{5}{2}$	Hyp. str. (and alt. int.)
55	Cs	133	$\frac{7}{2}$?	Hyp. str.
56	Ba	137	$\frac{3}{2}$?	Hyp. str.
	Ba	136, 138	0	
57	La	139	$\frac{5}{2}$	Hyp. str.
59	Pr	141	$\frac{5}{2}$	Hyp. str.
75	Re	187	$\frac{5}{2}$	Hyp. str.
	Re	189	$\frac{5}{2}$	
79	An	197	$\frac{9}{2}$?	Hyp. str.
80	Hg	199	$\frac{1}{2}$	Hyp. str.
	Hg	201	$\frac{3}{2}$	
	Hg	198, 200, 202, 204	0	
81	Tl	203	$\frac{1}{2}$	Hyp. str.
	Tl	205	$\frac{3}{2}$	
82	Pb	207	$\frac{1}{2}$	Hyp. str.
	Pb	204, 206, 208	0	
83	Bi	209	$\frac{9}{2}$	Hyp. str.

Many of the values of * should be accepted with considerable reserve.

In the particular case where the anti-symmetrical levels are not present at all, as in O_2 , then obviously $i = 0$. In other cases, where the a levels are present but weaker than the s levels, it is possible, by evaluating the relative intensities and allowing for the ordinary $(2J + 1)$ factor, to obtain a value for g_s/g_a and accordingly calculate i .

Investigations of some symmetrical diatomic molecules and their corresponding isotopic molecules ($Cl^{35}Cl^{35}$, $Cl^{35}Cl^{37}$; Li^6Li^7 , Li^6Li^7 ; $Bi^{79}Bi^{79}$, $Bi^{81}Bi^{81}$, $Bi^{79}Bi^{81}$) gave a striking demonstration of the correctness of Hund's theory. It was found that for the unsymmetrical molecules the intensities were no longer alternating, and for $Cl^{85}Cl^{37}$ were as regular as for CO.

When nuclear spins calculated from band spectra can be compared to those from hyper-fine structure (Li^7 , Br^{79} , B^{81}), the results agree.¹ This is satisfactory, for in the method of hyper-fine structure the measurements are precise and the interpretation sometimes not easy: while in alternating intensities the theory is beyond doubt, but the difficulty of measurement considerable.

(2) Rabi² has recently developed a method of measuring nuclear spins by an application of atomic rays. The only result so far to hand is $t = 3/2$ for Na. The method seems to have great possibilities. In Table VII are given some of the nuclear spins measured by the methods which have been described.

There are obvious difficulties in interpreting these data. The case of nitrogen whose nucleus has 14 protons, 7 electrons and a nuclear spin of 1, has led to the suggestion that only protons contribute to the resulting nuclear spin (each counting $1/2$). With this unexplained assumption, however, $Cl^{35} = 5/2$ and $F^{19} = 1/2$, remain facts so surprising that one would welcome both confirmatory and new experimental evidence. It is here that the nuclear spin of isotopes (Cl^{37} , for example) might give real illumination. Until this comes, it is perhaps enough to refer to the ingenious suggestion of Bartlett,³ who has built up hypothetical proton levels on the lines of the extra-nuclear electron levels [thus F^{19} is supposed to have a proton scheme similar to the electronic arrangement of Potassium ^2S : the total J value of the electron (J , in this case) is thus thought to be the same as the total i value of the protons]. It obtains some agreements which are remarkable if they are coincidences; but on the other hand, one or two of the more striking difficulties, such as that of the nitrogen nucleus, still remain.

¹ The results for bromine, however, are rather nebulous, and there is no completely satisfactory case where the two methods have been applied to the same nucleus.

² Rabi, *Phys. Rev.*, 43, 236, 1933.

³ Bartlett, *Phys. Rev.*, 42, 370, 1932.

CHAPTER XVII

THE SEPARATION OF ISOTOPES

131. 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 the elements in everyday use has been demonstrated, the possibility of their separation, to any reasonable extent, raises questions of some 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 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.

132. 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 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 :

$$\frac{x+y}{X+Y} = \frac{X}{X+Yr^{\frac{v}{v-\mu}}} + \frac{Y}{X+Yr^{\frac{\mu}{v-\mu}}}$$

where (X Y) (x, y) are the initial and final volumes of the gases, μ , v , 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

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

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, except those of hydrogen, 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—

$\frac{x+y}{X+Y} = \frac{1}{r^k}$ where $k = \frac{\nu - \mu}{\mu}$ a small quantity and, finally, the enrichment by diffusion of the residue as regards the heavier constituent may be expressed with sufficient accuracy by the expression

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

where m_1 , m_2 are the molecular masses of the lighter and heavier isotope respectively. In the case 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

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

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. 35 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.

By far the most important and spectacular success in the artificial separation of isotopes has been recently achieved by Hertz,¹ who had been working on the problem for some years. Gaseous diffusion through a special porous material at low pressures was employed and by means of an ingenious apparatus requiring no less than 24 mercury diffusion pumps this process was carried out continuously. Starting with normal neon which contains about 9 parts of isotope 20 to 1 part of isotope 22, Hertz was able to produce a light fraction in which the proportion of 22 was reduced below 1 per cent., and a heavy one in which the order was actually reversed and the proportion of 22 greater than that of 20 in the ratio 5:2. These fractions correspond to the unprecedented difference in atomic weight of 1.4

¹ *Natururisa.*, 26, 494 ; *Zeit. f. Physik.*, 79, 108, 1932.

of a unit. The changes in the constitution of the fractions was demonstrated by parabola mass-spectrum analysis and also by optical methods.

133. The separation of the isotopes of chlorine by the diffusion of HC1.—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 HC1 the 36th root is involved, and in that of HBr the 80th root. Although this is compensated to some extent by the larger percentage of the rarer isotope it is clear that the only way by which measurable increase in density may be hoped for will clearly be by increasing very largely the effective ratio of the initial to final volumes. This can be done by experiments on a huge scale or by a vast number of mechanical repetitions.

Harkins started to attack the HC1 problem in 1916¹ using the first of these two alternatives. In 1920 he mentions a quantity of 19,000 litres of HC1 as having been dealt with in these experiments.² In the following year³ he published numerical results indicating that a change in atomic weight of 0.055 of a unit had been achieved.

A full account of these operations was published in 1921,⁴ and later it was proved that chlorine with an atomic weight as low as 35.418 could be obtained.⁵

In a discussion on isotopes in 1921 Sir J. J. Thomson⁶ pointed out that a change in the molecular weight of HC1 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 exhaustively tried in the Cavendish Laboratory by E. B. Ludlam, but without success.⁷

134. Separation by Thermal Diffusion.—It has been shown on theoretical grounds independently by Enskog⁸ and Chapman⁹ 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

¹ Harkins, *Jour. Amer. Ghent. Soc.*, Feb., 1916.

² Harkins, *Science*, Mar. 19, 1920; *Nature*, April 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 Harkins and Hayes, *Jour. Amer. Chem. Soc.*, 43, 1803, 1921.

⁵ Harkins and Jenkins, *Jour. Amer. Chem. Soc.*, 48, 58, 1926.

⁶ J. J. Thomson, *Proc. Roy. Soc.*, **99A**, 98, 1921.

⁷ Ludlam, *Proc. Camb. Phil. Soc.*, **21**, 45, 1922.

⁸ Enskog, *Phys. Zeit.*, **12**, 538, **1911**; *Ann. d. Phys.*, 38, 750, 1912.

• Chapman, *Phil. Trans.*, **217A**, **115**, **1916**; *Phil. Mag.*, 34, 146, **1917**.

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,¹ and recently Ibbs² has demonstrated that the separation can be carried out continuously and that the time for equilibrium to be established is quite short.

Chapman has suggested³ 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

$$k_T = \frac{17}{3} \frac{m_2 - m_1}{m_2 + m_1} \frac{\lambda_1 \lambda_2}{9.15 - 8.25 \lambda_1 \lambda_2}$$

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 $k_T = 0.0095$. 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

$$\begin{aligned} \lambda_1 - \lambda'_1 &= -(\lambda_2 - \lambda'_2) = 0.0095 \log 800/80 \\ &= 0.022 \end{aligned}$$

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 n th power of the distance, the

¹ Chapman and Dootson, *Phil. Mag.*, 34, 248, 1917.

² Ibbs, *Proc. Roy. Soc.*, 99A, 385, 1921.

³ Chapman, *Phil. Mag.*, 38, 182, 1919.

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. The theory of thermal diffusion is discussed by R. S. Mulliken.¹

135. 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.² 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 layer convection is small. If it is small compared with diffusion the gases will separate to a certain extent. Since T is constant

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

$$\text{whence } \rho = \rho_0 e^{-\frac{Mg\Delta h}{RT}},$$

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 $K_0\rho_0$ at height h_0 , then their relative density at height $h_0 + \Delta h$ is given by

$$K = K_0 e^{-\frac{g\Delta h}{RT}(M_1 - M_2)}.$$

Putting $T = 220$ as is approximately true in England,

$$\frac{K}{K_0} = e^{-5.38 \times 10^{-7} \Delta h (M_1 - M_2)},$$

Δh being measured in kilometres. If $M_1 - M_2 = 2$, therefore

$$\frac{K}{K_0} = e^{-1.075 \times 10^{-6} \Delta h}.$$

¹ Mulliken, *Jour. Amer. Chem. Soc.*, 44, 1033, 1922.

² Lindemann and Aston, *Phil. Mag.*, 37, 530, 1919.

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

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

whence $\rho = \rho_0 e^{-\frac{Mv_0^2}{2RT}},$

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

$$K_0 e^{-\frac{v_0^2}{2RT}(M_1 - M_2)}.$$

A peripheral velocity of 10^5 cm./sec. or perhaps even 1.3×10^5 cm./sec. might probably be attained in a specially designed centrifuge,

so that $\frac{K}{K_0}$ might be made as great as $e^{-0.205(M_1 - M_2)}$ or even $e^{-0.37(M_1 - M_2)}$.

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 Poole¹ 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 0000015.

The first experiments on the separation of isotopes by the use of a centrifuge are those of Joly and Poole² who attempted to separate the hypothetical isotopic constituents of ordinary lead by this means.

¹ Poole, *Phil. Mag.*, 41, 818, 1921.

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

No positive results were obtained and the check experiments made with definite alloys of lighter metals with lead were by no means encouraging.

Mulliken¹ gives a complete theory of the separation of isotopes by thermal diffusion and by centrifuging, and shows that the latter method is likely to be of more value in the case of isotopes of high atomic weight. A special method, named evaporative centrifuging, is proposed whereby gas condensed in the periphery of the centrifuge at high speed would be allowed to evaporate very slowly, the light fractions being drawn off very gradually at low pressure from the centre of the apparatus. It is suggested that this method ought to yield a separation 10 to 15 times as great in one operation as would diffusion or evaporation. He also discusses the possibility of separating liquid isotopes by centrifuging. An attempt to test this theory in the case of mercury proved unsuccessful, and its failure is attributed to slight vibration of the centrifuge.

136. 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 fully from the theoretical standpoint by Lindemann. The thermodynamical considerations involved are the same in both cases. The reader is referred to the original papers² 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 βv ,³ which are the only practicable temperatures as far as lead is concerned, the difference of the vapour pressure and the constant of the laws of mass action may be expanded in powers of $\beta v/T$. The most important term of the type $\log (\beta v/T)$ is cancelled by the chemical constant if this is calculated by what seems the only reasonable way. The next term in $(\beta v/T)$ is cancelled by the 'Nullpunktsenergie' if this exists. All that remains are terms containing the higher powers of $\beta v/T$. 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."

¹ Mulliken, *Jour. Amer. Chem. Soc.*, 44, 1033, 1922 ; 45, 1592, 1923.

² Lindemann, *Phil. Mag.*, 37, 523, 1919 ; 38, 173, 1919.

³ βv is the "characteristic" and T the "Absolute" temperature.

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 report that the isotopes of lead could be separated by means of the Grignard reaction has been proved to be unfounded.¹ King² made careful and exhaustive attempts to separate the isotopes of mercury by chemical means. Six different reactions were studied but no separation was detected.

The negative result of the laborious efforts to separate the isotopes of neon by fractionation over charcoal cooled in liquid air has already been recounted.³ On the other hand, more recently Keesom and van Dijk⁴ have investigated the possibility of separating the isotopes of neon by rectification at or near its triple point. The vapour pressure curve for mixtures of isotopes as a function of composition calculated by Stern (not published) suggested that separation was practicable by this means. Using an elaborate rectifying column and distilling at -284.4°C . they succeeded in obtaining light and heavy fractions of densities corresponding to atomic weights 20.14 and 20.23 respectively, ordinary neon being taken as 20.18. They consider that these results satisfy the theory reasonably well and prove to a high degree of probability the very important conclusion that the solid state possesses zero-point energy.

Evaporation near the triple point was used by Urey, Brickwedde and Murphy⁵ to concentrate the hydrogen isotope of mass 2 to a point at which it was detectable spectroscopically. Further work on the vapour pressures of ordinary and enriched hydrogen has been published by Meissner and Steiner.⁶

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

¹Brennen, *Compt. Rend.*, **180**, 282, 1925; Richards, King and Hall, *J. Amer. Chem. Soc.*, **48**, 1530, 1926.

²King, *J. Amer. Chem. Soc.*, **49**, 1500, 1927. ³V. p. 33.

⁴Keesom and v. Dijk, *Proc. Kon. Akad. Wetan. te Amsterdam*, **34**, 1931.

⁵Urey, Brickwedde and Murphy, *Phys. Rev.*, **39**, 164; **40**, 1, 1932.

⁶Meissner and Steiner, *Zeit. f. Physik*, **79**, 601, 1932.

to 60° C. in the highest vacuum attainable. The evaporating and condensing surfaces were only 1 to 2 cm. 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 mercury² 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 delicacy with which it could be performed. With a 5 c.cm. pycnometer an accuracy of 1 part in 2,000,000 is claimed. The first figures published³ 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 1/100,000 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. These figures correspond to an isotopic moment of 1.40, in exact agreement with the result obtained by photometry of the mass-spectrum.⁵

Honigschmid and Birckenbach⁶ have examined the chemical atomic weight of samples of mercury of different density obtained by the method of Brlnsted and Hevesy with the following results :

	Density.	Atomic Weight.
Lightest fraction	0.999824	200.564 ± 0006
Ordinary mercury	1.000000	200.61 ± 0006
Heaviest fraction	1.000164	200.632 ± 0007

¹ V. p. 219. ² Groh and Hevesy, *Ann. der Phys.*, 63, 92, 1920.

³ Brdnsted and Hevesy, *Nature*, Sept. 30, 1920.

⁴ Brdnsted and Hevesy, *Phil. Mag.*, 43, 31, 1922.

⁵ V. p. 122. ⁶ Honigschmid and Birckenbach, *Ber.*, 56B, 1219, 1923.

The separation of the isotopes of mercury by this and analogous processes has been systematically studied by Mulliken.¹ Harkins and Madorsky^a describe a steel apparatus in which 2.5 kilograms of mercury can be dealt with in one operation. The mercury is contained in an annular trough surmounted by a Λ -shaped condensing surface. The latter is cooled with ice so that the fractions can be drawn off continuously without interrupting the distillation and the use of liquid air is eliminated. After 268 hours of operation with the large apparatus and 37 hours with a smaller glass one, they obtained a light fraction of 3.8 grs. of mercury, showing a decrease in atomic weight of 0.044 of a unit, and a heavy fraction of 4.4 grs. showing an increase of 0.052 of a unit.

This work has since been extended by Harkins and Mortimer.³ By means of still further technical improvements enabling increased speed of fractionation they have obtained two samples of mercury of about 100 grammes each which show a total difference of density corresponding to 0.189 of a unit of atomic weight.

138. Separation of the isotopes of chlorine by free evaporation.—Brønsted and Hevesy were able to announce the first separation of the isotopes of chlorine⁴ 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 sodium chlorides were taken and each precipitated with accurately the same volume of AgNO_3 solution, in slight excess. After precipitation and dilution to 2000 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

¹ Mulliken, *Jour. Amer. Chem. Soc.*, 44, 2387 ; 45, 1592, 1923.

² Harkins and Madorsky, *Nature*, 111, 148, 1923 ; *Jour. Amer. Chem. Soc.*, 45, 591, 1923.

³ Harkins and Mortimer, *Phil. Mag.*, 6, 601, 1928.

⁴ Brønsted and Hevesy, *Nature*, July 14, 1921.

showed that the difference in atomic weight of the two samples was 0.021, in good agreement with the density result.

139. Experiments on Zinc and other elements.—Experiments on the separation of the isotopes of zinc have been made by Egerton and Lee^x using the free evaporation method. In order to detect separation the densities of the end fractions were determined in the solid state. For this purpose they were cast in a vacuum and seeded with about 1 mg. of a particular kind of zinc. The first set of distillations gave a residue of slightly increased density, but the distillate was of the same density as the original zinc. The second set of distillations carried out under improved conditions yielded a residue showing a density increased by about 1 part in 3700 and a distillate of a density decreased by about 1 part in 3600. They discuss the possibility of attributing the difference of density to flaws, different physical conditions, or impurities, and show this to be unlikely.

With the isotopes of lead the method has not been so effective. Brönsted and Hevesy distilled lead chloride in a high vacuum. The end fractions were then submitted to atomic weight determinations by Honigschmid and Steinheil.² The results were 207.229 and 207.236, a difference too small in their opinion to warrant any claim for separation. A similar negative result has been recorded for the distillation of cadmium,³ ordinary lead, and a mixture of ordinary lead and uranium lead.⁴

More recently the method has been applied in an elegant manner by Hevesy and Logstrup⁵ to the interesting problem of the radioactivity of potassium. The pure metal was subjected to a prolonged series of fractionations at the end of which the atomic weight of the heaviest fraction was determined by Honigschmid and Goubeau to be 0.005 of a unit higher than that of ordinary potassium. Measurements of the radioactivity of this fraction showed that this property followed exactly the change in the percentage of the heavier isotope present. As potassium consists of isotopes 39 and 41 it was therefore to be concluded that the radioactivity was confined to 41 or some other unknown isotope heavier than 39.

140. Separation by mass-ray analysis.—The only method which seems to offer any hope of separating isotopes completely, and so obtaining pure specimens of the constituents of a complex element, is by analysing a beam of positive rays and trapping the particles

¹ Egerton and Lee, *Proc. Roy. Soc.*, 103A, 499, 1923.

² Honigschmid and Steinheil, *Ber.*, 56, 1931, 1923.

³ Sunier, *Abs. Theses*, Univ., Chicago, 4, 173, 1926-26.

⁴ Richards, King and Hall, *Jour. Amer. Chem. Soc.*, 48, 1530, 1926.

⁵ Hevesy and Logstrup, *Nature*, 120, 838, 1927; *Zeit. anorg. u. Chem.*, 171, 1, 1928.

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 is 0.01 radian. 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 0.005 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

$$0.005 \times 4 \times \frac{1}{2} \times \frac{1}{2} \times i = 0.005 i.$$

If i is as large as 5 milliamperes this is 1.5×10^4 E.S.U.

or
$$\frac{1.5 \times 10^4}{2.7 \times 10^{19} \times 4.77 \times 10^{-10}} = 1.2 \times 10^{-6} \text{ c.c./sec.,}$$

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 very small.

In the case of anode rays the conditions are more favourable. As has already been noted, by using suitable sources beams of ions of the alkali metals can be produced of intensity much greater than that in the normal discharge tube. If such beams are accelerated by a uniform field they can be rendered sufficiently homogeneous to allow of analysis by simple semicircular magnetic focussing.¹ An apparatus designed to produce specimens of pure isotopes 6 and 7 of lithium has been described by Morand.² He used an anode of

¹ V. p. 83.

² Morand, *Compt. Rend.*, **182**, 460, 1926; *Ann. de Physique*, **7**, **164**, 1927.

heated lithium salt, but although valuable measurements of the relative abundance of the isotopes were obtained, no success with the original problem was reported.

The element potassium is of interest in this connection, for its properties favour the production of intense beams of anode rays, and a complete separation of its isotopes, even in small quantities, would settle the important question of which isotope is the cause of its radioactivity. The separation of the lines of potassium does not need apparatus of great resolving power, and the collection of the particles can be made effectively, but the technical difficulties of maintaining intense beams over the long periods necessary for appreciable accumulation are very great. Apparatus for this purpose is now under construction in more than one laboratory and it is hoped that success will be reported in the near future.

141. Separation by photochemical methods.—An ingenious suggestion for separating the isotopes of chlorine has been made 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 HCl^{35} or HCl^{37} . Now ordinary chlorine contains about 3 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 photochemistry 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 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 negative.¹

A somewhat similar photochemical method has been applied recently by Kuhn and Martin.² Filtered light corresponding $\lambda > 2816179 \text{ \AA}$ the shortest and strongest component of $\text{COCl}^{35}\text{Cl}^{35}$ was allowed to fall upon a stream of $\text{COCl}^{35}\text{Cl}^{35}$ vapour mixed with iodine. The chlorine resulting from the photochemical dissociation was caught with HgI_2 and its atomic weight determined. Two experiments gave 35.428 and 35.430 respectively. A control with ordinary light gave 35.455. The difference corresponds to about one-fifth of the theoretical.

142. Separation by Ionic Migration.—It was first suggested by Lindemann³ that if isotopic ions were allowed to migrate freely through a substance like gelatine, the head of the migrating column might be expected to contain a preponderance of the lighter isotope. Experiments on these lines have been undertaken by several observers, but so far without success. In the experiments of Kendall and Crittenden⁴ the conditions were so arranged that the ions moved in an agar-agar gel at the rate of 12 to 18 inches a day. Quantitative separation of sodium iodide from sodium thiocyanate was obtained after a movement of only a few feet, but there was no indication of any separation in the case of sodium chloride even after a movement of 100 feet. Murmann⁵ describes many attempts to separate isotopes by this and other methods. All gave negative results and he concludes that ionic mobilities are dependent only on atomic volume and not on atomic weight.

143. Separation by Electrolysis.—The possibility of this method has been suggested⁶ but no success has been described until, quite recently, it has been applied to the exceptional case of hydrogen with the most striking results. Lewis⁷ reports that by electrolysing water he has been able to increase the proportion of the hydrogen isotope of mass 2 to such an extent as to give a sample of water of density 1.035. This astonishing achievement gives promise of the preparation of approximately pure H^2 in the not too distant future and thus opens a most fascinating new field in chemistry.

144. Other methods of separation and general conclusions.—The following methods have also been suggested: Electron impact

¹ Merton and Hartley, *Phil. Mag.*, 43, 430, 1922.

² Kuhn and Martin, *Naturwiss.*, 42, 772, 1932.

³ Lindemann, *Proc. Roy. Soc.*, **99A**, 103, 1921; Pilley, *Nature*, **111**, 848, 1923.

⁴ Kendall and Crittenden, *Proc. Nat. Acad. Sci.*, 9, 75, 1923.

⁵ Murmann, *Oesterr. Ghent. Ztg.*, 26, 14, 1923.

⁶ Kendall and Crittenden, *Proc. Nat. Acad. Sci.*, 9, 75, 1923.

⁷ Lewis, *Jour. Amer. Chem. Soc.*, 55, 1297, 1933.

in a discharge tube in the case of inert gases, the lighter atoms being more strongly urged towards the anode.

The action of light on metallic chlorides.¹

Fractional crystallization.²

In no case has any certain success been reported.

A survey of the separations actually achieved so far shows that from the practical point of view they are, with two exceptions, 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 the quantities produced are insignificant.

The remarkable successes with neon by continuous diffusion, and with hydrogen by electrolysis are, however, in a different category and foreshadow the most interesting developments in the future.

¹ Renz, *Zeit. Anorg. Chem.*, 116, 62, 1921.

² Atkinson, *Nature*, 112, 283, 1923 ; Robinson and Briscoe, *Jour. Chem. Soc.*, 127, 138, 1925.

APPENDIX I

TABLE OF PACKING FRACTIONS AND ISOTOPIC WEIGHTS

Atoms marked + were measured by Bainbridge, x by Costa, o by means of optical spectra. The others by means of the second mass.spectrograph.

Symbol.	Mass Number.	Packing Fraction.	Isotopic Weight.	Proportional error x 10*.	Symbol.	Mass Number	Packing Fraction.	Isotopic Weight.	Proportional error x 10*.
H	1	+ 77.8	1.00778	1	Se	78	. 8	77.937	2
H+	2	+ 67.5	201351	1	Se	80	. 7.3	79.941	1
He	4	+ 5.4	400216	0.5	Br	79	. 90	78.929	0.5
Li ^x	6	+ 200	6012	3	Br	81	. 8.6	80.926	0.5
Li ^x	7	+ 170	7012	3	Kr	78	. 9.4	77.926	1
Be+	9	+ 17.2	90155	1	Kr	80	. 91	79.926	1
B	10	+ 13.5	100135	0.5	Kr	82	. 8.8	81.927	0.5
B	11	+ 100	110110	0.5	Kr	83	. 8.7	82.927	0.5
C	12	+ 30	120036	0.3	Kr	84 i	. 8.5	83.928	0.5
CO	13	+ 30	130039	5	Kr	86	. 8.2	85.929	0.5
N	14	+ 5.7	14.008	1	Nb	93	. 8	92.926	5
NO	15	(2)	(15.007)	?	Mo	98	. 5.5	97.945	5
O	16		160000	—	Mo	100	. 5.5	99.945	5
Oo	17	+ 1.7	170029	0.2	Sn	120	. 7.3	119.912	1
OO	18	+ 3.6	180065	0.2	Te	126	. 5	125.937	2
F	19	00	190000	0.3	Te	128	. 5	127.936	2
Ne+	20	. 0.16	19.99671	0.5	I	127	. 5.3	126.932	1
Ne+	22	. 0.24	21.99473	0.5	Xe	134	. 5.3	133.929	1
Si	28	. 6.5	27.9818	1	Cs	133	. 5	132.933	2
P	31	. 5.6	30.9825	0.5	Ba	138	. 61	137.916	2
Cl	35	. 4.8	34.983	0.5	Ta	181	. 4	180.927	3
Cl	37	. 50	36.980	0.5	W	184	0	18400	5
A	36	. 6.6	35.976	0.5	Re	187	. 1	186.981	2
A	40	. 7.2	39.971	0.3	Os	190	. 1	189.981	3
Cr	52	. 100	52.948	3	Os	192	. 1	191.981	3
Ni	58	. 100	57.942	2	Hg	200	+ 0.8	200016	1
Zn	64	. 9.9	63.937	3	Tl	203	+ 1.8	203036	2
As	75	. 8.8	74.934	0.5	Tl	205	+ 1.8	205037	2

APPENDIX II

TABLE OF ISOTOPES AND THEIR PERCENTAGE ABUNDANCE

Figures for abundance in ordinary type indicate some form of direct measurement though their accuracy varies widely. Italics indicate rough estimates or indirect calculations from chemical atomic weights. *S* indicates that the element is simple.

Symbol.	Mass Number.	Abund- ance.	Symbol.	Mass Number.	Abund- ance.	Symbol.	Mass Number.	Abund- ance.
H	1	99.9	Al	27	<i>S</i>	Mn	55	<i>S</i>
	2	0.003		28	<i>94</i>		54	<i>95</i>
He	4	<i>S</i>		29	<i>4</i>	Fe	56	<i>5</i>
			Si	30	<i>2</i>		59	<i>S</i>
Li	6	8.3	P	31	<i>S</i>	Ni	58	<i>66</i>
	7	91.7		32	<i>96</i>		60	<i>34</i>
Be	(8)	(0.05)	S	33	<i>1</i>	Cu	63	<i>68</i>
	9	99.9		34	<i>3</i>		65	<i>32</i>
B	10	20		35	<i>76</i>	Zn	64	<i>50.4</i>
	11	80	Cl	37	<i>24</i>		66	<i>27.2</i>
C	12	99.75		36	<i>0.6</i>		67	<i>4.2</i>
	13	0.25	A	40	<i>99.4</i>		68	<i>17.8</i>
N	14	99.86		39	<i>5.4</i>		70	<i>0.4</i>
	15	0.14	K	41	<i>94.6</i>	Ga	69	<i>60</i>
O	16	99.81		40	<i>98.6</i>		71	<i>40</i>
	17	0.03	Ca	44	<i>1.4</i>	Ge	70	<i>21.2</i>
	18	0.16		45	<i>S</i>		72	<i>27.3</i>
F	19	<i>S</i>	Ti	48	(<i>S</i>)		73	<i>7.9</i>
			V	51	<i>S</i>		74	<i>37.1</i>
Ne	20	90.4		50	<i>4.9</i>		76	<i>6.5</i>
	21	0.6	Cr	52	<i>81.6</i>	As	75	<i>S</i>
	22	9.0		53	<i>10.4</i>		74	<i>0.9</i>
Na	23	<i>S</i>		54	<i>3.1</i>		76	<i>9.5</i>
							77	<i>8.3</i>
Mg	24	77.4					78	<i>24.0</i>
	25	11.5					80	<i>48.0</i>
	26	11.1					82	<i>9.3</i>

TABLE OF ISOTOPES AND THEIR PERCENTAGE ABUNDANCE (*continued*)

Symbol. •	Mass Number.	Abund- ance.	Symbol.	Mass Number.	Abund- ance.	Symbol.	Mass Number.	Abund- ance.
Br {	79	50	In	115	<i>S</i>	Pr	141	<i>S</i>
	81	50						
Kr {	78	0.42	Sn	112	1.07	Nd {	142	34
	80	2.45		114	0.74		144	33
	82	11.79		115	0.44		146	33
	83	11.79		116	14.19	Ta	181	<i>S</i>
	84	56.85		117	9.81			
	86	16.70		118	21.48	W {	182	22.6
Rb {	85	75		119	11.02		183	17.3
	87	25		120	27.04		184	30.2
Sr {	86	10.0		121	2.96		186	29.9
	87	6.6	Sb {	122	5.03	Re {	185	38.2
	88	83.4		123	6.19		187	61.8
Y {	89	<i>S</i>	Te {	121	56	Os {	186	1.0
				123	44		187	0.6
Zr {	90	59		122	2.9		188	13.4
	92	12		123	1.6		189	17.4
	94	24		124	4.5		190	25.1
	(96)	(5)		125	6.0		192	42.5
Nb {	93	<i>S</i>		126	19.0	Hg {	196	0.10
				(127)	?		197	0.01
Mo {	92	14.2		128	32.8		198	9.89
	94	10.0	I {	130	33.1		199	16.45
	95	15.5		127	<i>S</i>		200	23.77
	96	17.8	Xe {	124	0.08		201	13.67
	97	9.6		126	0.08		202	29.27
	98	23.0		128	2.30		203	0.006
Ru {	100	9.8		129	27.13		204	6.85
	96	5		130	4.18	Te {	203	29.4
	98	?		131	20.67		205	70.6
	99	12		132	26.45	Pb {	203	0.04
	100	14		134	10.31		204	1.50
	101	22	Ca {	136	8.79		205	0.03
Ag {	102	30		133	<i>S</i>		206	27.75
	104	17	Ba {	135	5.9		207	20.20
Cd {	107	51		136	8.9		208	49.55
	109	49		137	11.1		209	0.85
	110	14		138	74.1		210	0.85
	111	12	La {	139	<i>S</i>	Bi	209	<i>S</i>
	112	24						
	113	10	Ce {	140	90	U	238	<i>S</i>
	114	35		142	10			
	116	5						

APPENDIX III

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 sur-

PERIODIC TABLE

I H 1-0078				
Valency 0	I +1	II +2	III +3	IV +4
2 He <i>4-002</i> 4	3 Li <i>6-940</i> 6, 7	4 Be <i>9-02</i> 9	5 B <i>10-82</i> 10, 11	6 C <i>12-00</i> 12, 13
10 Ne <i>20-183</i> 20, 21, 22	11 Na <i>22-997</i> 23	12 Mg <i>24-32</i> 24, 25, 26	13 Al <i>26-97</i> 27	14 Si <i>28-06</i> 28, 29, 30
18 Ar <i>39-944</i> 36, 40	19 K <i>39-10</i> 39, 41 29 Cu <i>63-57</i> 63, 65	20 Ca <i>40-08</i> 40, 44 30 Zn <i>65-38</i> 64, 66, 67, 68, 70	21 Sc <i>45-10</i> 45 31 G <i>69-72</i> 69, 71	22 Ti <i>47-90</i> 48 32 Ge <i>72-60</i> 70, 72, 73, 74, 76
36 Kr <i>83-7</i> 78, 80, 82, 83, 84, 86	37 Rb <i>85-44</i> 85, 87 47 Ag <i>107-880</i> 107, 109	38 Sr <i>87-63</i> 86, 87, 88 48 Cd <i>112-41</i> 110, 111, 112, 113, 114, 116	39 Y <i>88-92</i> 89 49 In <i>114-8</i> 115	40 Zr <i>91-22</i> 90, 92, 94, 96 50 Sn <i>118-70</i> 112, 114, 116, 117, 118, 119, 120, 121, 122, 124
54 Xe <i>131-3</i> 124, 126, 128, 129, 130, 131, 132, 134, 136	55 Cs <i>132-81</i> 133	56 Ba <i>137-37</i> 135, 136, 137, 138	57 La <i>138-92</i> 139	
58 Ce <i>140-13</i> 140, 142	59 Pr <i>140-92</i> 141	60 Nd <i>144-27</i> 142, 144, 146	61—	62 Sm <i>150-43</i> 152-0
63 Eu <i>157-3</i>	64 Gd <i>157-3</i>	65 Tb <i>169-2</i>	66 Dy <i>162-46</i>	67 Ho <i>163-6</i>
68 Er <i>167-64</i>	69 Tm <i>169-4</i>	70 Yb <i>173-5</i>	71 Lu <i>175-0</i>	72 Hf <i>178-6</i>
	73 Ta <i>181-8</i>	74 W <i>183-84</i>	75 Re <i>186-207</i>	76 Os <i>190-23</i>
	77 Ir <i>192-22</i>	78 Pt <i>195-08</i>	79 Au <i>197-2</i>	80 Hg <i>200-61</i> 196, 197, 198, 199, 200, 201, 202, 203, 204
	81 Tl <i>204-39</i> 203, 205	82 Pb <i>207-22</i> 203, 204, 205, 206, 207, 208, 209, 210	83 Bi <i>208-98</i>	84 Po <i>209</i>
86 Rn <i>222-0</i>	87—	88 Ra <i>226-97</i>	89 Ac	90 Th <i>232-12</i>

APPENDIX III

rounded by a thick line. The properties of the missing elements can be predicted with 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; 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.

OF THE ELEMENTS

V -3	VI -2	VII -1	VIII		
7 N 14.008 14, 15	8 O 16.000 16, 17, 18	9 F 19.00 19			
15 P 31.02 31	16 S 32.06 32, 33, 34	17 Cl 35.457 35, 37			
23 V 50.95 51	24 Cr 52.01 50, 52, 53, 54	25 Mn 54.93 55	26 Fe 55.84 54, 56	27 Co 58.94 59	28 Ni 58.69 58, 60
33 As 74.93 75	34 Se 79.2 74, 76, 77, 78, 80, 82	35 Br 79.916 79, 81			
41 Nb 93.3 93	42 Mo 96.0 92, 94, 95, 96, 97, 98, 100	43 —	44 Ru 101.7 96, 98, 99, 100, 101, 102, 104	45 Rh 102.9	46 Pd 106.7
51 Sb 121.76 121, 123	52 Te 127.5 122, 123, 124, 125, 126, 128, 130	53 I 126.92 127			
73 Ta 181.4 181	74 W 184.0 182, 183, 184, 186	75 Re 186.31 185, 187	76 Os 190.8 186, 187, 188, 189, 190, 192	77 Ir 193.1	78 Pt 195.23
83 Bi 209.00 209	84 Po	85 —			
91 U X H	92 U 238.14 238				

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