ATOMIC AND NUCLEAR CHEMISTRY

VOLUME 1

ATOMIC THEORY AND STRUCTURE OF THE ATOM

by

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TO CONSTANCE

FOREWORD

THE GRADUAL development of modern atomic theory is one of the most fascinating stories in the history of scientific discovery. Yet, there is a substantial body of scientific opinion which favours the presentation of atomic theory in terms of contemporary ideas on nuclear structure and the wave mechanics of electrons in atoms. Of course, no study is complete until this manner of treatment has been covered, and it is perfectly valid to develop the theory thus, based on the neutron–proton model of nuclear structure. But, the student who is satisfied with this approach and does not enquire further into the origins of these ideas misses a great deal. There is a temptation with overloaded syllabuses to attempt to forge ahead as rapidly as possible casting aside the work of nineteenth-century pioneers as material of interest solely to the historians. Such an approach is probably encouraged by those who misinterpret remarks of authority, such as the classic one attributed to Dirac, that " wave mechanics has explained most phenomena in physics and the whole of chemistry ".

Mr. Peacocke presents the arguments for a more enlightened outlook on the subject in this book. The exciting developments in classical atomic chemistry during the nineteenth century, portray in a very real sense the difficulties which are common to the gradual unfolding of any new approach to scientific theory and the reluctance of men to accept new ideas until their support is undeniable. This situation is vividly illustrated in the first two chapters. There follows an account of the work of the early atomic physicists in which their discoveries are related to modern ideas on the chemistry of atoms. The essential results of the simple wave mechanical treatment are summarised at the end of Chapter 5 and at this stage the earlier exposition of Bohr's atomic model becomes significant.

The author is best known for his development of experimental methods in radiochemistry for sixth forms. Those who have visited the science department at St. John's School must have been impressed by the enthusiasm of the young scientists and with the comprehensive range of experiments they perform in the upper school. The results achieved by this enlightened approach to sixth-form chemistry are obvious in the school's record of successes in the Oxford and Cambridge scholarships examinations and the long list of first class honours later achieved by the pupils at the end of their university careers.

The publication of this first volume of *Atomic and Nuclear Chemistry* will give masters at other schools an opportunity to follow in detail part of the course which has become almost a tradition at St. John's, Leatherhead. However, the real value of the work will not be fully appreciated until the appearance of the second volume in which the majority of the radiochemistry experiments will appear.

Keble College, Oxford. DENNIS F. SHAW.
September, 1967.

PREFACE

IN WRITING this book an attempt has been made to present the modern ideas of the atomic theory and atomic structure against the background of their historical development. The author feels strongly that students of science should know how the present-day theories have developed and something about the men who developed them. There is a tendency today to regard the early work as of interest to historians only. This is an extremely dangerous view and could easily give students the impression that current theories were complete and final. The author feels that a true perspective can only be obtained by following the logical development of our present ideas. In addition, he feels that reading about the achievements of the early workers, often with primitive equipment, will act as a source of inspiration and help the research worker of the future to realise that if he wishes to advance the frontiers of knowledge he must have an infinite capacity for taking pains.

The first five chapters follow a chronological order where possible, so that each new discovery fits in to the general pattern. The final chapter has been treated somewhat differently in the interest of clarity. In many cases some brief notes on the character and personality of the great scientists who are mentioned have been included, so that they may be seen as real people and not mere names.

Though the book was not written with any particular examinations in mind, it is intended to be of use to students taking the advanced and scholarship levels of the General Certificate of Education, university entrance scholarships and college preparatory courses. It would also be of use to first-year university students, to those taking chemistry as a subsidiary subject, and to others who may wish to study the original work in this field, but may not have the time or the facilities to consult the original papers.

Chemists will say that much of this book is physics, and on traditional grounds this is true. However, many people today feel that a fusion of chemistry and physics is desirable. The projected Nuffield course of physical science is an attempt to achieve this, and it is hoped that this book may be of particular use to those who will follow such a course.

To give an accurate account of the experiments described in the text the original papers have been consulted, in particular the following:

The Proceedings of the Royal Society
The Journal of the Chemical Society
The Journal of the American Chemical Society
Carnegie Publication 125, 1910
Radioactivity by Rutherford
Isotopes by Aston
Atoms by Perrin

Many other works have been studied and it is impossible to record all those which have left their impression on the author's mind. In particular, he would like to express his debt to *Physical Chemistry* by Glasstone, *A History of Chemistry* by Partington, and *Inorganic Chemistry* by Emeleus and Anderson.

The following have kindly given permission to reproduce diagrams or questions:

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Imperial College of Science and Technology, questions taken from scholarship papers.

The author wishes to express his thanks to Dr. J. E. Spice for reading the manuscript and for his helpful advice, to his two colleagues, Mr. W. O. Clarke and the Rev. J. L. Birley for many helpful suggestions, to the Rank Organization for supplying the photograph of Moseley's original apparatus for the determination of atomic number, to Messrs. International Nickel for supplying a copy of their periodic table, to his many students who have tested experiments described in the text, and to Miss J. C. Foxwell for typing the manuscript. Last, and by no means least, he wishes to thank Dr. D. F. Shaw for reading the manuscript and the proofs, for discussions and for making a number of most helpful suggestions.

The author wishes to make it clear that he accepts full responsibility for all the statements made in this book.

CHAPTER 1

CLASSICAL ATOMIC THEORY

Origin of the atomic theory

THE IDEA of atoms was originally developed by the ancient Greek philosophers. Leukippos is supposed to have been the first to put forward an atomic hypothesis about 500 B.C. and it was greatly extended by Demokritos. Unfortunately most of their original writings have disappeared. The great philosopher Aristotle, who conceived the four-element theory, was opposed to the idea of atoms for he could not accept the principle of empty space. Such was his reputation that his view prevailed over the theory of Demokritos and for nearly 2000 years the atomic theory suffered eclipse.

Interest was revived by a controversy between Gassendi and Descartes around A.D. 1600. Gassendi supported the atomic theory while Descartes opposed it. Boyle believed in atoms and so did Newton, who used the theory to explain Boyle's law by assuming a gas to be composed of minute particles which repelled each other with a force varying inversely as the square of the distance. Before the time of Newton we can at best regard the atomic theory as a speculative philosophy not based on observed fact. Newton was the first man to make an attempt to explain observed facts by the use of this theory.

John Dalton, 1766–1884

The atomic theory as we know it today was conceived in the mind of Dalton. Dalton was a very remarkable man. Born of Quaker parents he opened his own school at the age of 12 although history records that he had some difficulty in keeping the older boys in order. The school soon closed but he started another with his brother 3 years later. He spent much time in the study of mathematics and particularly the works of Newton, which probably gave him the ideas which he later developed into his atomic theory. He spent most of his life in Manchester and became Professor of Mathematics at New College, Manchester, in 1793.

Dalton began his scientific work as a meteorologist, studying the properties of the atmosphere. He produced his law of partial pressures in a paper published in 1801 in which he stated that " in any mixture of gases the total pressure is the sum of the partial pressures exerted by each gas ". It is now regarded as practically certain that Dalton put forward his atomic theory as a result of his experiments on mixed gases. He conceived his famous law of multiple proportions, the cornerstone of the atomic theory, in his mind and then proceeded to test it by experiments on the reaction of nitric oxide with air over water in narrow tubes (0·3 in. diameter) and wide jars. In the narrow tube he admitted 36 measures of nitric oxide and then passed in 100 measures of air. After a few minutes he found that 80 measures of nitrogen were left. In the wide jars he admitted 72 measures of nitric oxide and again passed in 100 measures of air. This was followed by a momentary agitation whereupon he again found 80 measures of nitrogen left. From these experiments he concluded that oxygen may combine with a certain proportion of nitric oxide or with twice that proportion, but with no intermediate quantity.

The actual figures were probably much less accurate than he implies, for Dalton was a poor experimentalist and he must have rounded them off to suit his theory. The results he obtained were fortuitous and were caused by his method of working.

In the narrow tube with limited access to water, nitric oxide and oxygen react to form nitrogen dioxide, and the relatively slow reaction goes to completion:

$$2NO+O_2 \rightarrow 2NO_2$$

The nitrogen dioxide is absorbed by the water to form nitric and nitrous acids

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

In the wide jar, however, half of the nitric oxide is rapidly oxidised to nitrogen dioxide which then reacts with the rest of the nitric oxide in the presence of water to form nitrous acid:

$$NO_2 + NO + H_2O \rightarrow 2HNO_2$$

The figures obtained in the second experiment are due to the fact that the nitric oxide had free access to water owing to the previous agitation, whereas in the narrow tube the nitric oxide was largely screened from the water by the air. In view of Dalton's subsequent rejection of Gay-Lussac's law it is strange that he should have used volume reactions as his first illustration of the law of multiple proportions.

Dalton supported his law by an analysis of marsh gas (methane) and olefiant gas (ethylene) in which he showed that the weights of carbon combining with a fixed weight of hydrogen were in the ratio of 1 : 2. Other chemists, notably Thomas Thomson and J. J. Berzelius, soon found many other instances of the law of multiple proportions and it was quickly established as a great generalization.

The laws of chemical combination

The three laws of chemical combination were all announced between 1799 and 1802. The law of constant composition or definite proportions — " All pure chemical compounds contain the same elements united in the same proportions by weight " — was first stated by Proust, a Frenchman who was Professor of Chemistry in Madrid from 1789 to 1808 when his laboratory was wrecked during the siege. The law was challenged by Berthollet who stated that certain metals, notably lead and tin, could combine with oxygen over a wide range of proportions, but Proust maintained that these alleged compounds were really mixtures of certain definite oxides. The views of Proust prevailed over those of Berthollet and until comparatively recently fixity of composition was regarded as a unique feature of a chemical compound.

Modern work has shown that compounds of fixed composition are probably to be regarded as the limiting case. Any compound consisting of discrete molecules identical in the solid and vapour or solution must have an invariable composition, but in the case of crystalline compounds variable composition is the rule rather than the exception though the variations are often very small. These variations are due to imperfections in the crystal and variable valency. When crystallisation occurs at a high temperature atomic vibrations result in vacant sites in the crystal. Even potassium chloride prepared by crystallisation from the melt may show up to 0·4% departure from its ideal formula, though when crystallised from aqueous solution it will have its true composition. The widest departure from ideal stoichiometric proportions is shown by elements of the transitional series in combination with sulphur. The well-known compound ferrous sulphide, often the first compound shown to a chemistry student, varies in composition from FeS to $FeS_{1\cdot 14}$. This is made possible by the variable valency of iron. Some of the iron atoms are in the ferric state so that vacancies in the crystal sites can occur. Many other sulphides and oxides show these variations. Even in the oxides of lead at least two non-stoichiometric forms exist between PbO, Pb_3O_4 and PbO_2. Non-stoichiometric compounds are referred to as Berthollide compounds as opposed to Daltonide compounds which strictly conform to Proust's law.

The law of multiple proportions: " When two elements combine to form more than one compound, the weights of one which react with a fixed weight of the other are in the ratio of small whole numbers." This law really only holds for simple inorganic compounds, for when it is applied to organic chemistry or to complex silicate structures and silicones the ratio is not a small whole number at all. This departure from the law is not as serious as it sounds for it is due to the large number of atoms in the molecules concerned. However, it is improbable that the law would have been recognised by Dalton if his knowledge of organic chemistry had been extensive.

The law of equivalent or reciprocal proportions: " When two elements A and B react with a third C, then the weights of A and of B which react with a fixed weight of C are in the proportions in which they react with each other or a simple multiple of these proportions " was first clearly recognised by Richter. Richter was a German mathematician who was also a chemist and his alert mind was able to summarise much earlier work in the above generalisation though he stated it in much more complex terms. The term " equivalent " was probably first used by Cavendish and he showed that acids and bases reacted in equivalent proportions. Cavendish was a brilliant experimentalist, but not noted for his contributions to chemical theory. His work provided the material for Richter to elaborate into a chemical law. Even as stated above, the law is far from clear and Fig. 1.1 and the following example may help to a better understanding. Consider the elements hydrogen, oxygen and magnesium to illustrate the A, B and C of Richter's law.

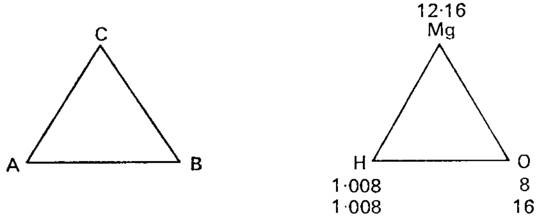

FIG. 1.1.

When magnesium displaces hydrogen from an acid, 1·008 g of hydrogen are displaced by 12·16 g of magnesium. 8·000 g of oxygen react with 12·16 g of magnesium to form magnesium oxide. 1·008 g of hydrogen react with 8·000 g of oxygen to form water or with 16·000 g of oxygen to form hydrogen peroxide. The numbers 8 : 16 are in the simple ratio of 1 : 2. Many other examples could be chosen and an almost endless series of triangles can be built on to the above three elements, e.g. hydrogen, oxygen and carbon; magnesium, oxygen and nitrogen, to give but two instances.

Dalton's atomic theory

As explained on page 2, Dalton is believed to have conceived his atomic theory in his mind and then used the laws of chemical combination to support his theory. In its original form the theory was stated as follows:

(i) Elements are composed of minute indivisible particles called atoms.
(ii) All the atoms of a given element are of the same size and weight.
(iii) Compounds are formed of compound atoms.
(iv) Atoms unite in small whole numbers.

It will be immediately clear that the above four postulates completely explain the laws of chemical combination. Apart from minor challenge the first three postulates remained the guiding principles of chemistry for over 100 years. The fourth postulate had to be modified with the growth of organic chemistry, but it was only during the present century that modifications had to be made to the other three. These modifications can be summarised briefly as follows:

(i) Atoms are no longer considered to be indivisible, but they do not divide in chemical reactions. They may lose one or more electrons, but the nucleus of the atom remains unchanged. An atom can now be defined as the ultimate particle of an element.
(ii) This postulate can no longer be accepted owing to the discovery of isotopes. The term " isotope " was invented by Frederick Soddy and means " the same place ". Isotopes are elements of different nuclear masses which occupy the same place in the periodic table (Chapter 2) and so have the same nuclear charge. An element is now considered to be characterised by the positive charge on its nucleus.
(iii) The only modification necessary to this postulate is to substitute " molecules " or " ions " for " compound atoms ".

Dalton invented a system of symbols and attempted to write formulae but his formulae were very complex. They had, however, an advantage over the formulae used by the alchemists in that they at least showed the number of atoms of each element present in the molecule. In fact, many of Dalton's formulae were incorrect because he had not got sufficient data. He made use of certain empirical rules, his approach being essentially statistical. If two elements combined to form only one compound he assumed that compound to be binary, i.e. of the form AB. If, on the other hand, the elements formed two different compounds he assumed that one was binary, i.e. AB and the other ternary, i.e. A_2B or AB_2. As he knew only one compound between hydrogen and oxygen he wrote the formula for water as HO. He did not use our present system of symbols but a series of circles and crosses to represent the different elements. Methane and ethylene using modern symbols were represented as CH_2 and CH respectively. He also drew up a table of the relative weights of atoms. This table was in reality a table of reacting weights and not atomic weights at all and it was far from accurate, for, as mentioned previously, Dalton was a poor experimentalist.

The combination of gases by volume

In 1808 Gay-Lussac, who was Professor of Chemistry at the École Polytechnique and also Professor of Physics at the Sonborne, a most careful and accurate experimentalist, published his famous law of combining volumes: " When two gases combine, their volumes are in a simple ratio, and they bear a simple ratio to the volume of the product if this is gaseous, provided that the temperature and pressure remain constant." This law was well supported by experiment but presented Dalton with a difficulty. Gay-Lussac showed that one volume of hydrogen plus one volume of chlorine gave two volumes of hydrogen chloride gas. Now Dalton assumed that equal volumes of gases contained equal numbers of atoms following the ideas of Newton, and Gay-Lussac's law meant that the atoms of hydrogen and of chlorine must have been split in order to produce two compound atoms of hydrogen chloride. Dalton replied with a spirited denial. " The truth is ", he said " gases do not combine in simple ratios by volume. When they appear to do so it is caused by experimental error." This denial of experimental fact was all the more extraordinary in view of Dalton's own work on his reaction of nitric oxide with oxygen in which he used volume relations to prove his law of multiple proportions. In fact it brought him into disrepute.

Avogadro's hypothesis

In 1811 the problem was solved by the Italian physicist Avogadro, who published his famous hypothesis in which he suggested that the ultimate particles of gases need not necessarily be single atoms but might be even numbers of atoms, i.e. what we should call molecules, and in this case they could divide. Avogadro, who lived and died in Turin, became Professor of Mathematical Physics at the University. He was little known in Italy and still less abroad. His hypothesis was published in French in the *Journal de Physique* and very little attention was paid to it until it was revived by Cannizaro about 40 years later. The failure to recognise Avogadro's hypothesis resulted in great confusion on the question of atomic weights and until it was accepted several different formulae could be written for the same compound depending on the values taken for the respective atomic weights.

The work of Berzelius

The ideas of Dalton were greatly extended by J. J. Berzelius. Berzelius was a Swede and was born in Stockholm in 1779 where he spent most of his life. Apart from his work on the atomic theory his improvements of chemical techniques were remarkable. He invented rubber tubing, test tubes and test-tube racks, gravimetric filter paper and platinum crucibles; he introduced the use of desiccators and calcium chloride for drying gases; last, but by no means least, he invented our modern system of symbols. By a long series of careful analyses he tested and proved the laws of chemical combination. He published the first comprehensive tables of atomic weights and his final table produced in 1828 contained similar values to those we use today; yet a few years later they were all discredited. The reason for this was that the leading chemists realised that Berzelius's atomic weights depended largely on his own intuition and did not rest on any solid basis.

Berzelius used Dalton's rules (p. 7) coupled with the law of Dulong and Petit: " Specific heat × atomic weight = 6·4 approximately ", and Mitscherlich's law of isomorphism: " Substances which crystallise in the same form have the same chemical formula." Unfortunately both of these laws were empirical in that they could only be tested by using values of atomic weights which themselves had no sound foundation. Berzelius also used vapour density measurements to fix atomic weights. He assumed that equal volumes of elementary gases contained equal numbers of atoms and determined the relative weights of atoms of gaseous elements by comparing the weights of equal volumes. He accepted Gay-Lussac's law as an experimental fact but he would not accept Avogadro's hypothesis because it conflicted with his dualistic theory. The dualistic theory assumed that all compounds were made up of two parts, the one positive and the other negative. He was led to this view largely by the work of Davy, the pioneer of electro-chemistry who isolated the alkali metals.

Berzelius explained Gay-Lussac's law by assuming that when hydrogen and chlorine combine to form hydrogen chloride the volume occupied by the hydrogen chloride molecule was twice the volume occupied by either the hydrogen or the chlorine atoms. This led him to write the equation

$$\mathrm{H+Cl = HCl}$$

since the two volumes of hydrogen chloride formed from one volume of hydrogen and one volume of chlorine meant to Berzelius that one compound atom (molecule) of hydrogen chloride was formed from one atom of hydrogen and one atom of chlorine.

Berzelius obtained the correct atomic weights for the diatomic elementary gases, but was led into difficulty with such elements as mercury, phosphorus and sulphur* having respectively one, four and eight atoms in the molecule and his first table of atomic weights gave mercury 100, phosphorus 62 and sulphur 128. Later he corrected these values by making various assumptions. His greatest difficulty concerned the atomic weight of carbon. According to the law of Dulong and Petit the atomic weight of carbon appeared to be 6, but Berzelius gave it its present value of 12, though he had no sound basis for this assumption at all.

In 1830 the French chemist Dumas, famous for his classical research on the composition of water by weight (Fig. 6.12), discovered organic replacement in which hydrogen was replaced by chlorine in organic compounds. Berzelius could not accept that an electro-negative element like chlorine could replace an electro-positive element like hydrogen and yet maintain the essential constitution of the compound. The controversy raged for some years but finally it became quite clear that organic substitution must be accepted and the dualistic theory was discredited. With the collapse of his theory all Berzelius's atomic weights were discarded because chemists felt that his figures rested largely on his own intuition.

Cannizaro's solution

During the next 25 years great confusion existed over the formulae of compounds, and papers published during this time are most difficult to follow. Some chemists took the atomic weight of oxygen as 8, following Dalton, whilst others followed Berzelius and took the figure of 16. In December 1860 a German chemist named Lothar Meyer summoned a conference at Karlsruhe at which the main workers in different countries met. No agreement was reached as is frequently the case at international conferences. The language problem was acute, there being no interpreters. The conference was about to break up in confusion when a young

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* Sulphur also forms S_6, S_4, and S_2, the proportions of the four species varying with temperature.

Italian chemist, by name Cannizaro, distributed a paper in which he revived Avogrado's hypothesis and redefined atomic weight as " the least weight of an element to be found in the molecular weights of any of its compounds ". This provided a sound theoretical basis for determining atomic weights. When Lothar Meyer read Cannizaro's paper he is reported to have said " the scales fell from my eyes, doubts vanished, and a feeling of calm certainty came in their place ". Cannizaro's argument can be summarised in the following way. One volume of hydrogen plus one volume of chlorine forms two volumes of hydrogen chloride and by applying Avogadro's hypothesis it is clear that the hydrogen molecule must contain an even number of atoms. Hydrogen chloride, when dissolved in water, forms a mono-basic acid, i.e. giving rise to only one series of salts, and so must have only one atom of hydrogen in its molecule. Since two molecules of hydrogen chloride are formed from one molecule of hydrogen, clearly there must be only two atoms in a hydrogen molecule. This is further supported by the experimental fact that one volume of hydrogen never gives rise to more than two volumes of any

TABLE 1.1

Compound	Molecular weight	Weight of carbon in the molecular weight
Methane	16	12
Ethylene	28	24
Acetylene	26	24
Carbon dioxide	44	12
Butane	58	48
Benzene	78	72
Turpentine	136	120

The lowest common factor of the numbers in column 3 is seen to be 12. 12 is therefore the atomic weight of carbon. No matter how many carbon compounds are analysed no sub-multiple of 12 is ever found in their molecular weights.

gaseous products, so the hydrogen molecule cannot divide beyond two. He also showed conclusively the connection between vapour density and molecular weight. Vapour density is defined as the weight of a given volume of the gas compared with the weight of the same volume of hydrogen under the same conditions of temperature and pressure. By applying Avogadro's hypothesis this means the weight of one molecule of the gas compared to the weight of one molecule of hydrogen. Since the molecule of hydrogen contains only two atoms the molecular weight of the gas must be twice its vapour density. This gave a sure method for the determination of molecular weights, i.e. the relative weights of the molecules of a substance to the weight of one atom of hydrogen. An example of the use of Cannizaro's absolute method can be given in the determination of the atomic weight of carbon (Table 1.1).

It was possible to apply Cannizaro's method to a considerable number of elements and thus to check Dulong and Petit's law and Mitscherlich's law of isomorphism and prove them to be correct. Berzelius's table of atomic weights, which he had published in 1828, was now brought back into use. It is sad to think that the great chemist had died 12 years earlier without seeing his work finally accepted.

EXPERIMENTS

1.1. TO ILLUSTRATE THE LAW OF MULTIPLE PROPORTIONS BY FORMATION OF THE TWO CHLORIDES OF COPPER

Weigh about 0·5 g of copper foil* in a weighed boiling tube to an accuracy of 1 mg. Dissolve the copper foil in the minimum of concentrated nitric acid, holding the boiling tube at an angle to avoid loss of spray. This should be performed in a fume cupboard. Evaporate the excess nitric acid gently and decompose the nitrate by ignition to cupric oxide. Dissolve the cupric oxide in about 5 ml of concentrated hydrochloric acid.

* The copper foil must not be too thin or disintegration will result during the second part of the experiment.

Weigh a second piece of copper foil, which should be about 1 g, in a weighing bottle or on a clock glass and drop the foil into the boiling tube. Boil gently in the fume cupboard for a few minutes. Extract the foil with a glass rod and holding it with tongs wash with a few drops of water into the boiling tube and dry. Weigh the foil. Insert it again into the boiling tube, boil for another minute, withdraw, wash and weigh as before. Repeat the operation to constant weight. Compare the loss in weight of the second piece of foil to the weight of the first piece. These two weights should be equal. Pour the contents of the boiling tube into cold water in a beaker. White cuprous chloride should precipitate with no trace of blue colour.

1.2. ILLUSTRATION OF GAY-LUSSAC'S LAW, BY REACTING AMMONIA WITH A GIVEN VOLUME OF CHLORINE AND MEASURING THE RESIDUAL VOLUME OF NITROGEN

Fit a well-rolled bark cork or rubber bung to a burette. Test the burette for gas tightness by evacuating the burette with a water pump through the tap. Mark the position of the cork with a chinagraph pencil and then measure the volume of the dead space above and below the scale by running in water from another burette.

Empty out the water, refill with brine and then fill the burette with chlorine by inverting it over a mortar filled with brine and bubbling in chlorine in a fume cupboard. The chlorine can be conveniently generated by dropping concentrated hydrochloric acid into a small flask containing potassium permanganate. Make sure that all the air has been displaced from the flask by chlorine before filling the burette.

When all the brine has been displaced, insert the cork into the open end of the burette under the brine and place the burette, tap uppermost, into a tall jar of water which should be a few degrees above the temperature of the lab. If the burette cannot be completely immersed, turn it tap down in the jar and again invert to bring the whole burette to the desired temperature. Open the tap momentarily to allow some chlorine to escape into the air and to bring the gas to atmospheric pressure at the temperature of the jar.

Withdraw the burette and open the tap under some 0·880 ammonia solution in a small beaker. The slight cooling produced by withdrawing the burette from the levelling jar should result in ammonia being sucked in. If ammonia does not go in, cool the outside of the burette by swabbing with a piece of cotton wool soaked in acetone. Do not introduce more than 1 or 2 ml of ammonia; close the tap securely. A vigorous reaction starts and when the burette is inverted a small flame will be seen travelling along the tube.

When the reaction is complete, open the tap under some 1–2 M sulphuric acid containing an indicator such as methyl red. This is to neutralise the excess ammonia. Invert the burette and repeat until no more acid enters, then return it to the levelling jar, check the temperature and adjust if the water has cooled more than two or three degrees. Bring the burette to the temperature of the water in the levelling jar, open the tap under the water and level off the residual volume of nitrogen. Compare this volume to the original volume of chlorine. The ratio should be 1 : 3·00. The experimental error is of the order of 1 %. This experiment can also be used for proving the formula for ammonia. Thus, three volumes of chlorine yield one volume of nitrogen. Applying Avogadro's law, three molecules of chlorine yield one molecule of nitrogen. Three molecules of chlorine react with six atoms of hydrogen and therefore six atoms of hydrogen were combined with one molecule or two atoms of nitrogen, which gives ammonia the empirical formula of NH_3. The molecular formula follows from the vapour density and hence the molecular weight.

QUESTIONS

1.1. An element X gives four oxides which contain 76·2, 68·0, 61·4 and 56·1 % of X respectively. Show that these figures agree with the law of multiple proportions and deduce a possible atomic weight for X.

1.2. How would you demonstrate the Laws of Multiple and Reciprocal proportions in as many ways as possible for compounds involving the elements iron, hydrogen, oxygen and sulphur? Give an outline of the actual experiments you would propose to carry out. [Oxford Schol.]

1.3. State (*a*) Avogadro's Hypothesis, (*b*) Gay-Lussac's Law, and explain their importance. Explain fully why we believe the formula of hydrogen gas to be H_2. [Oxford Prelim.]

1.4. " Gay-Lussac's notion of measures [volumes] is analogous to mine [Dalton's] of atoms, and if it could be proved that all gases have the same number of atoms in the same volume, the two hypotheses would be the same, except that mine is universal and his applies only to gases." Discuss the ideas, truths and fallacies contained in this statement. [Imperial College Schol.]

1.5. To what extent is the Atomic Theory based on laws of chemical combination that can be tested experimentally? [Oxford Schol.]

CHAPTER 2

THE CLASSIFICATION OF THE ELEMENTS

Soon after Berzelius's atomic weight tables were published attempts were made to find a connection between atomic weight which seemed to be fundamental, and chemical properties. In 1829 Döbereiner published his law of triads in which he stated that in any group of three closely related elements the properties of the middle element were intermediate between those of the first and third and the atomic weight was the arithmetic mean of the other two. He gave as examples the three triads lithium, sodium, potassium : calcium, strontium, barium : chlorine, bromine, iodine. Thus:

$$\begin{array}{lll}
\mathrm{Li} = 7 & \mathrm{Ca} = 40 & \mathrm{Cl} = 35{\cdot}5 \\
\mathrm{Na} = 23 & \mathrm{Sr} = 87{\cdot}6 & \mathrm{Br} = 80 \\
\mathrm{K} = 39 & \mathrm{Ba} = 137{\cdot}4 & \mathrm{I} = 127 \\
\frac{7+39}{2} = 23 & \frac{40+137{\cdot}4}{2} = 88{\cdot}7 & \frac{35{\cdot}5+127}{2} = 81{\cdot}3
\end{array}$$

Similar results were quoted for oxygen, sulphur and selenium.

Little attention was paid to this observation at the time partly because there were other groups of triads such as As, Sb, Bi and Zn, Cd, Hg which did not conform to the law. Another and more important reason was that Berzelius's atomic weights were soon discredited and confusion existed for many years on this subject.

The next attempt at classification was due to Newlands who published his law of octaves in 1864. He stated that if the elements beginning with lithium were arranged in order of their atomic weights the properties recurred after the eighth element "like the eight notes in an octave of music". His table was arranged somewhat as follows:

						H
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca					

Unfortunately he weakened his theory by attempting to extend it beyond calcium. The next element, scandium, had not been discovered at this time and titanium, which in the absence of scandium comes next in order after calcium, showed little resemblance to aluminium, and differences became even more marked as the series continued. The paper which he read to the Chemical Society was ridiculed and Professor Carey Foster asked Newlands if he had ever thought of " arranging the elements in the order of their initial letters!" Newlands replied modestly that he had tried several other schemes but this seemed to be the most effective. Publication of his paper was refused, but 20 years later Newlands received the Davy medal of the Royal Society.

The periodic law

Five years later, in 1869, the periodic law was announced simultaneously and independently by Lothar Meyer in Germany and Mendele'ef in Russia. Mendele'ef's exposition was more precise. He stated that " the properties of the elements are periodic functions of their atomic weights ". So convinced was he of the truth of the law that he left gaps for missing elements, notably scandium, gallium and germanium, naming them Eka-boron, Eka-aluminium and Eka-silicon respectively. He stated where they would probably be found and predicted their properties with astonishing accuracy. When his predictions were confirmed by the discovery of these three elements the success of his theory was assured. Table 2.1 compares the predicted properties of Eka-silicon with those actually found for germanium.

TABLE 2.1.

	Eka-silicon (Es) Predictions of Mendele'ef	Germanium (Ge) Actual properties
Atomic weight	72	72·60
Specific gravity	5·5	5·35
Colour	Dirty grey	Greyish white
Action of air	Will give a white powder of the oxide, EsO_2, on calcination in air	Gives the oxide, GeO_2, as a white powder on calcination in air
Action of water	Element will decompose steam with difficulty	The element does not decompose water
Action of acids	Slight	Not attacked by hydrochloric acid, but is attacked by aqua regia
Alkalis	No marked action	Solutions of caustic potash do not affect it, but it is oxidised by fused caustic alkalis
Preparation	The action of sodium on EsO_2 or K_2EsF_6 will give the element	The reduction of GeO_2 with carbon, or of K_2GeF_6 with sodium yields the element
Properties of the oxide	The oxide, EsO_2, will be refractory and will have sp.gr. 4·7. It will be less basic than TiO_2 or SnO_2, but more basic than SiO_2	The oxide, GeO_2, is refractory. Its sp. gr. is 4·703 and its basic properties are feeble
Hydroxide	The hydroxide will be soluble in acids and the solutions so formed will readily decompose, forming a hydroxide	Acids do not precipitate the hydroxide from dilute alkaline solutions, but from concentrated solutions acids precipitate GeO_2 or a hydroxide
Chloride	The chloride, $EsCl_4$, will be a liquid with b.p. $<$ 100°C and a sp.gr. of 1·9 at 0°C	The chloride, $GeCl_4$, is a liquid of b.p. 83°C and density 1·879
Fluoride	The fluoride, EsF_4, will not be gaseous	The fluoride, GeF_4, is a gas
Ethyl compound	Eka-silicon will form a compound, $Es(C_2H_5)_4$ boiling at 160°C and of sp.gr. 0·96	Germanium forms a compound, $Ge(C_2H_5)_4$. Its m.p. is 90°C and its b.p. is 163·5°C. Its sp.gr. is 0·9911

Atomic volume

Lothar Meyer made a most important contribution by drawing attention to the periodicity of atomic volumes. Atomic volume is defined as the ratio atomic weight/density. When the atomic volume is plotted against the atomic weight the curve shown in Fig. 2.1 is obtained.

It will be noted that the alkali metals form the peaks of the curve and, in general, similar elements occupy similar positions. Strict agreement could not be expected for several reasons:

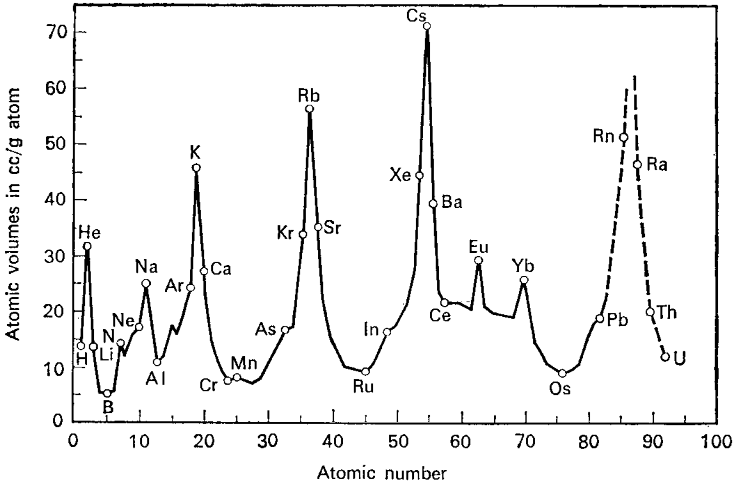

FIG. 2.1. Atomic volumes of the elements.

1. The densities of the elements should all be measured at the same temperature and in the solid state. This is very difficult, if not impossible, for the inert gases, and the density in the liquid state has to be used.
2. Certain elements exist in different allotropic forms which have different densities, e.g. yellow phosphorus density 1·83, violet phosphorus density 2·34, and diamond density 3·51, graphite density 2·5. The position of the element will change according to the allotrope chosen.

TABLE 2.2. PERIODIC TABLE OF THE ELEMENTS
Atomic numbers thus, 7. Atomic weights thus, 6·94

Group	I		II		III		IV		V		VI		VII		VIII	O
	a	b	a	b	a	b	a	b	a	b	a	b	a	b		
Period 1														H 1. 1·008		He 2. 4·003
Period 2	Li 3. 6·94		Be 4. 9·01			B 5. 10·82		C 6. 12·00		N 7. 14·01		O 8. 16·00		F 9. 19·00		Ne 10. 20·18
Period 3	Na 11. 22·99		Mg 12. 24·32		Al 13. 26·98			Si 14. 28·09		P 15. 30·98		S 16. 32·07		Cl 17. 35·46		A 18. 39·94
Period 4	K 19. 39·10	Cu 29. 63·54	Ca 20. 40·08	Zn 30. 65·38	Sc 21. 44·96	Ga 31. 69·72	Ti 22. 47·90	Ge 32. 72·60	V 23. 50·95	As 33. 74·91	Cr 24. 52·01	Se 34. 78·96	Mn 25. 54·94	Br 35. 79·92	Fe 26. 55·85 Co 27. 58·94 Ni 28. 58·71	Kr 36. 83·80
Period 5	Rb 37. 85·48	Ag 47. 107·88	Sr 38. 87·63	Cd 48. 112·41	Y 39. 88·92	In 49. 114·82	Zr 40. 91·22	Sn 50. 118·70	Nb 41. 92·91	Sb 51. 121·76	Mo 42. 95·95	Te 52. 127·61	Tc 43. [99]	I 53. 126·91	Ru 44. 101·1 Rh. 45 102·9 Pd 46. 106·4	Xe 54. 131·30
Period 6	Cs 55. 132·91	Au 79. 197·0	Ba 56. 137·36	Hg 80. 200·61	Rare Earths La 57. 138·92 Lu 71. 174·99	Tl 81. 204·39	Hf 72. 178·50	Pb 82. 207·21	Ta 73. 180·95	Bi 83. 209·00	W 74. 183·86	Po 84. 210	Re 75. 186·22	At 85. [210]	Os 76. 190·2 Ir 77. 192·2 Pt 78. 195·09	Rn 86. 222
Period 7	Fr 87. [223]		Ra 88. 226		Ac 89. 227		Th 90. 232·05		Pa 91. 231		U 92. 238·07					

Rare Earths:	Ce 58,	Pr 59,	Nd 60,	Pm 61,	Sm 62,	Eu 63,	Gd 64,	Tb 65,	Dy 66,	Ho 67,	Er 68,	Tm 69,	Yb 70,	Lu 71
	140·13	140·92	144·27	(147)	150·35	152·0	157·26	156·93	162·51	164·94	167·27	168·94	173·04	174·99

For the synthetic elements the atomic weight of the principal isotope is given in brackets.

The periodic table

A later form of Mendele'ef's periodic table, with the inclusion of the noble gases, discovered by Ramsay about 1900, is reproduced as Table 2.2. The main features can be summarised as follows:

1. The elements are arranged horizontally in periods numbered 1 to 7. The number of elements in each period are 2, 8, 8, 18, 18, 32, incomplete. It will be noted that the numbers, 2, 8, 18, 32 are twice the squares of the natural numbers, i.e. $2\times1^2, 2\times2^2, 2\times3^2, 2\times4^2$.

2. The table is divided vertically into nine groups numbered I–VIII and 0. The groups I–VII are subdivided into *a* and *b* subgroups from period 4 onwards.

3. The elements in periods 2 and 3 are called the typical elements. Groups Ia and IIa resemble the typical elements, whereas Ib and IIb show little resemblance. Groups IIIb to VIIb resemble the typical elements whereas IIIa–VIIa show little resemblance. In group VIII lateral resemblances are very marked.

4. The elements on the left side of the table are strongly electro-positive whereas those on the right side are strongly electro-negative. This and several of the following points are shown more clearly in a modern version of the periodic table (facing p. 140).

5. The most electro-positive element is bottom left whereas the most electro-negative element is top right. In groups Ia, IIa, IIIb–VIIb electro-positive character increases with increasing atomic weight, whereas this trend is clearly reversed in groups Ib, IIb and VIII.

6. In periods 4, 5 and 6 the elements scandium to zinc, yttrium to cadmium and hafnium to mercury, which do not resemble the typical elements, are called transitional elements since they form a bridge between the elements in groups Ia, IIa, and IIIb–VIIb which resemble the typical elements. They have certain particular characteristics:

(*a*) Strong lateral resemblances.

(*b*) Variable oxidation states (see p. 23 for a definition of oxidation state).

(*c*) Marked catalytic activity.

(*d*) Formation of coloured ions.

(*e*) Tendency to form complex ions.

(*f*) Paramagnetism rising to a maximum in group VIIa. (A paramagnetic substance in a magnetic field becomes magnetised parallel to the field, whereas a diamagnetic substance is magnetised antiparallel.)

7. In period 6 will be found a group of fourteen elements, cerium to lutecium, called the " Rare earths " or " Lanthanides ", which show such a marked resemblance in chemical properties that it is extremely difficult to separate them. The original method of separation depended on the fractional crystallization of their sulphates — a long and tedious process, and only comparatively recently by the use of ion exchange techniques has it been possible to obtain high purity specimens.

8. Diagonal relationships. These are particularly marked in periods 2 and 3. Thus lithium resembles magnesium in chemical properties even more than sodium. Lithium forms an almost insoluble carbonate, no solid bicarbonate is known, the fluoride is insoluble and the reaction of the metal with water is comparatively slow. Beryllium shows resemblances to aluminium. The oxide is amphoteric, the element does not decompose steam and the chloride is extremely hygroscopic. Boron shows resemblances to silicon. It is a typical non-metal, forms an acidic oxide, a series of hydrides and volatile halides.

9. Oxidation states. The term " oxidation state " is used here in the sense of " numerical " valency. Valency can no longer be used in this restricted sense and has come to mean the nature of the bonding, which can only be determined by the measurement of inter-atomic distances. It is clearly undesirable to use one word to describe two essentially different ideas (valency is discussed in detail in the volume *Chemical Binding and Structure* of this series).* When one element combines with a more electronegative element it is said to be oxidised. Reduction is the

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* J. E. Spice, *Chemical Binding and Structure*, Pergamon Press, 1964.

opposite. Oxidation state may be defined as the number of atoms of hydrogen or fluorine or half the number of atoms of oxygen which will combine with one atom of the element. Elements can have negative oxidation states as well as positive oxidation states. When an element combines with a more electro-positive element (reduction) it is said to have a negative oxidation state. Thus fluorine will have an oxidation state of -1 in F_2O, since oxygen is electro-positive with respect to fluorine. Nitrogen in ammonia has an oxidation state of -3. Hydrogen in metallic hydrides has an oxidation state of -1. Thus oxidation is brought about by an increase in the oxidation state and reduction by a decrease in the oxidation state.

Relation of oxidation state to group number. In the second period the oxidation state of the element is fixed and is equal to the group number, or 8 minus the group number (ignoring the sign of the oxidation state). Thus Li = 1, Be = 2, B = 3, C = 4, N = 3, O = 2, F = 1. There are a few exceptions to this rule. Thus carbon in carbon monoxide has an oxidation state of 2. Nitrogen in the oxides of nitrogen varies in oxidation state from 1 to 5, thus N_2O (1) NO (2) N_2O_3 (3) N_2O_4 (4) N_2O_5 (5). Nitrogen can never have a covalency of 5, since its valency electrons are in the second quantum level which cannot accommodate more than eight electrons (p. 81), but nitrogen has clearly been oxidised when N_2O_4 is converted to N_2O_5. The term " oxidation state " is seen here to be particularly descriptive. In the third period the maximum oxidation state is equal to the group number. Thus Na = 1, Mg = 2, Al = 3, Si = 4, P = 5, S = 6, Cl = 7. The first four elements show fixed oxidation states, but phosphorus can have oxidation states of 3 and 5 in PCl_3 and PCl_5, sulphur 2, 4 and 6 in SCl_2, SCl_4 and SF_6, and chlorine 1, 4, 6 and 7 in Cl_2O, ClO_2, ClO_3 and Cl_2O_7.

In periods 4 to 7 the maximum oxidation state corresponds, with a few exceptions to the group number. As mentioned on page 21, the transitional elements show variable oxidation states with a maximum corresponding to the group number except in group VIII. The only member of this group to show an oxidation state of 8 is osmium in the tetroxide OsO_4. The elements in subgroups Ia, IIa, IIIb–VIIb normally have fixed oxidation states corresponding to the group number, but lower oxidation states are also known, e.g. tin and lead in $SnCl_2$ and $PbCl_2$, group Vb in which an oxidation state of 3 is marked, and the halogens bromine and iodine which exhibit a marked oxidation state of -1. Iodine is the only member of this group apart from chlorine to show an oxidation state of 7 (periodic acid and iodine heptafluoride).

10. Anomalous character of the elements in period 2. The first member of any group often shows marked differences to the other members of that group. Reference has already been made to this under the heading of diagonal relationships where some of the differences shown by lithium, beryllium and boron to the remainder of their group members were cited. Carbon in group IV does not show unexpected differences except perhaps in the hydrides; in fact, the elements carbon, silicon, germanium, tin, lead show a steady gradation in properties from a typical non-metal to a typical metal. Nitrogen, on the other hand, shows marked differences from the remaining elements in group Vb. It is inert whereas the other elements are reactive. It forms a diatomic molecule whereas phosphorus, arsenic and probably antimony form tetratomic molecules. It does not show allotropy. It forms three hydrides and five oxides. There is no counterpart to hydrazoic acid HN_3 or to the oxides N_2O and NO. The oxide N_2O_3 is monomeric and very unstable whereas the corresponding oxides of phosphorus, arsenic and antimony are stable and have a dimeric tetrahedral structure. Nitrogen pentoxide in the solid state exists as nitronium nitrate NO_2^+ ʃNO_3^-, in this respect resembling solid phosphorus pentachloride, which exists as PCl_4^+ ʃPCl_6^-. The pentoxides of phosphorus and arsenic have a tetrahedral dimeric structure, P_4O_{10}, As_4O_{10}. The trihalides of nitrogen, except NF_3, are explosive whereas the trihalides of the other elements in the group are stable.

Oxygen shows fundamental differences to the remaining members of the group. Its normal dimeric molecule is quite different from the eight-membered sulphur molecule. Liquid oxygen is paramagnetic. The one allotrope of oxygen — ozone — is endothermic with respect to oxygen and unstable at all temperatures, quite different from the enantiotropic forms of sulphur, rhombic and monoclinic, which can exist in equilibrium at a temperature which varies with the pressure. Water resembles hydrogen sulphide in formula, but is far less volatile, whereas from molecular weight considerations it should be far more volatile. The only resemblance shown between H_2O and H_2S is the appearance of the solids. Solid hydrogen sulphide is pure white and resembles snow. The low volatility of water is caused by association brought about by hydrogen bonding. (Hydrogen bonding is discussed in the volume *Chemical Binding and Structure* of this series.) Oxygen combines with the other members of group VI in a manner which is not shown by any other first-row element. The properties of oxygen are so divergent from the remainder of the group that it is hardly profitable to attempt a comparison.

Fluorine shows much greater resemblance to the other members of its group than is shown by nitrogen or oxygen, but it still has anomalous properties. Hydrogen fluoride is less volatile than hydrogen chloride whereas it should be more volatile. Like water it is associated through hydrogen bonding. The fluorides show anomalous solubilities. Thus calcium fluoride is insoluble and silver fluoride soluble, unlike the corresponding chlorides, bromides and iodides. Nitrogen trifluoride, as mentioned on page 24, is stable and very different in character from nitrogen trichloride. Though the other halogens are very reactive, fluorine is the most reactive element known, attacking every other element except the noble gases helium, neon and argon. Owing to the small size of the fluoride ion and the extreme reactivity of the element, fluorine brings out the highest covalency in all elements. Thus sulphur forms SF_6, the only compound in which sulphur is linked directly with six other atoms and iodine forms IF_7. Osmium was formerly supposed to yield an octafluoride OsF_8 but the existence of this compound now seems very doubtful. Apart from these differences the chemistry of fluorine closely resembles the chemistry of the rest of the group.

11. The position of hydrogen. Hydrogen stands apart from all the other elements. At one time it was customary to place hydrogen in group I, but it shows little resemblance to the alkali metals. The ionisation energy of hydrogen, i.e. the energy required to convert 1 gram of hydrogen gas in the form of atoms into 1 gram atom of hydrogen ions is 314 kcal. This compares with 124 kcal for lithium and 401 kcal for fluorine. (See p. 89 and question 5.5.) In this case hydrogen shows greater resemblance to the halogens than the alkali metals. It must be clearly understood that free hydrogen ions only exist in gaseous discharge tubes. In chemical systems the hydrogen ion is always solvated and in water exists as H_3O^+. If gaseous hydrogen chloride is dissolved in anhydrous toluene with which the hydrogen ion cannot combine, normal acidic properties are absent. Thus the solution has no action on litmus, marble or magnesium (see expt. 2.3).

The compounds of hydrogen with the halogens are quite different from the alkali metal halides. Hydrogen does, indeed, form negative ions in the metal hydrides such as lithium hydride, which is a crystalline salt-like compound, but reacts immediately with water to form lithium hydroxide and hydrogen gas. The peculiar properties of hydrogen are due to the atomic structure, with a single electron surrounding the proton, and the strong tendency to form covalent compounds.

12. Formation of ions. Positive ions are formed more easily with increasing atomic volume whereas the converse is true for the formation of negative ions. A glance at the atomic volume curve (Fig. 2.1 on page 19) will show the truth of this statement. In general the tendency to form ions increases with descent of a periodic group. The maximum positive charge on any ion is four and is shown by Sn^{4+} and Pb^{4+}, whereas the maximum negative charge on a simple ion is two as in S^{2-}. Iodine, which normally forms a negative ion, can form positive ions as in iodine monochloride. The reason for this will become clear after studying atomic structure (Chapter 4).

13. Order of atomic weights. The periodic law of Mendele'ef shows certain anomalies. Thus argon and potassium, cobalt and

nickel, tellurium and iodine are out of order. The properties of argon and potassium fix their relative positions and the same applies to a lesser degree for the other two pairs. Much effort was spent in redetermining the atomic weights of these elements in an attempt to reconcile them with the periodic law, but to no purpose. Their position remained anomalous until the discovery of atomic numbers as explained in Chapter 4.

EXPERIMENTS

2.1. PROPERTIES OF TRANSITIONAL ELEMENTS

(a) Variable oxidation states and differently coloured ions

(i) Dissolve 1–2 g of ammonium vanadate in 50–100 ml of water. The salt is sparingly soluble and forms a colourless solution. Add 5–10 ml of dilute sulphuric acid. The solution turns yellow, the characteristic colour of the vanadate ion VO_2^+ (oxidation state 5). Pour the solution into a 250 ml stoppered bottle containing about 20 g of fresh zinc amalgam and shake, examining the colour of the solution at intervals. The colour will change first to blue vanadyl VO^{2+} (oxidation state 4), then to green vanadic V^{3+} (oxidation state 3), and finally to violet vanadous V^{2+} (oxidation state 2). With a little practice it is possible to stop at the appropriate colour change. The changes are most striking and quickly demonstrated.

(ii) Dissolve 2 g of potassium or sodium dichromate in 50 ml of concentrated hydrochloric acid. Pour the solution into a 250 ml flat-bottomed flask fitted with a two-holed cork and bent delivery tube arranged to dip beneath the surface of water in a beaker. In the other hole insert a bent glass tube which goes to the bottom of the flask (Fig. 2.2). Add about 20 g of granulated zinc to the flask and quickly replace the cork, allowing the hydrogen to bubble away beneath the surface of the water. The solution first turns to green chromic (oxidation state 3) and then to blue chromous (oxidation state 2). The chromous ion is highly unstable and is immediately oxidised to green chromic if any air is admitted to the flask. Chromous salts, with the exception of chromous acetate, must be prepared in the absence of air. Chromous acetate is sparingly soluble and can be precipitated by blowing the solution in the flask into a saturated solution of sodium acetate with the aid of carbon dioxide. Chromous acetate is red.

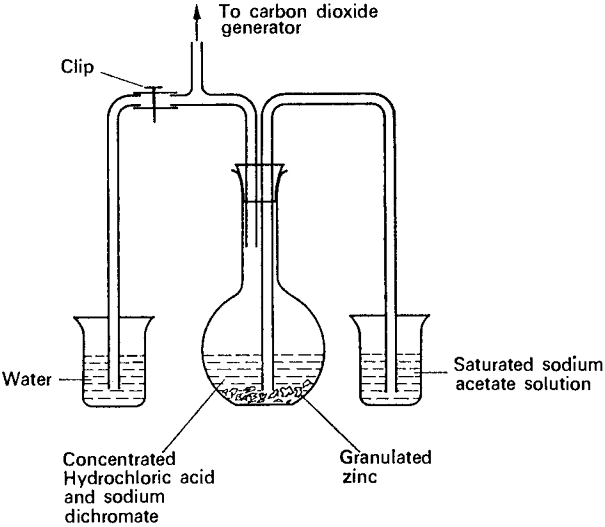


Fig. 2.2. Apparatus to prepare chromous acetate.

(*b*) *Catalytic activity*

Pour 20 ml of 100 volume hydrogen peroxide into a 250 ml measuring cylinder and add a few millilitres of a colloidal solution of a metal such as gold, silver or platinum, or add a little manganese dioxide. A rapid evolution of oxygen will result.

(*c*) *Formation of a complex ion*

Preparation of nickel tetrammine nitrite. Dissolve 6 g of nickel acetate in the minimum of water (35 ml) containing a little dilute acetic acid to prevent hydrolysis. Warm gently to dissolve the salt but do not heat above 30°C or loss of acetic acid will result and a basic salt may precipitate.

Dissolve 30 g of ammonium acetate and 20 g of sodium nitrite in 50 ml of water. Warm gently but keep the temperature below 30°C. Mix the two solutions and cool to about 15°C, using ice if necessary. Add 15 ml of 0·880 ammonia solution and stir with a mechanical stirrer for about 1 hr. Fine red crystals of the complex salt soon start to separate. Leave the solution to stand for some hours and then transfer the crystals to a suction filter, washing them on to the filter with ethanol. Wash the crystals with more ethanol which dissolves excess ammonium acetate and sodium nitrite, and dry in air. Yield about 4 g.

Place some of the crystals on a watch-glass in an empty desiccator and pour 0·880 ammonia solution into the bottom of the desiccator. Leave overnight. The violet hexammine will form. It is unstable in air and soon reverts to the stable red tetrammine by loss of ammonia.

2.2. PARAMAGNETISM OF LIQUID OXYGEN

Blow a light glass bulb of about 0·5 cm diameter with a short neck. Cool the bulb by dipping into liquid oxygen and then fill with the liquid. Suspend with a piece of cotton between the poles of a powerful electromagnet. Set the bulb vibrating gently across the field. The vibration will change direction and the bulb will vibrate parallel to the field.

An even simpler way of showing that oxygen is paramagnetic is to arrange the poles of the electromagnet about 0·5 in. apart and to pour liquid oxygen over the poles. The liquid oxygen is held between the poles and gives the appearance of a diabolo. It rapidly evaporates, but if the current is switched off the remaining liquid falls to the bench top.

2.3. PROPERTIES OF HYDROGEN CHLORIDE IN THE ANHYDROUS STATE

Place about 100 ml of toluene over calcium chloride for a day or two in a corked flask and then filter into a 100 ml stoppered cylinder or bottle. Arrange an apparatus to generate dry hydrogen chloride and bubble the gas through the toluene until it appears to be saturated. Pour the solution of hydrogen chloride in toluene on to a piece of marble and a strip of magnesium in two separate flasks. Note the complete absence of reaction. Add a little water to each flask. The magnesium and marble will immediately react. Test the solution of hydrogen chloride in toluene with dry blue litmus paper and then damp the paper. The paper will turn red.

QUESTIONS

2.1. Describe the principal features of the periodic classification of the elements. Give a brief explanation of the classification in terms of modern ideas of atomic structure. [O. & C. G.C.E.]

2.2. Discuss the advantages and disadvantages of the periodic system of classification of the elements as put forward by Mendele'ef. To what extent have the disadvantages disappeared with the introduction of the present-day method of classification? [Imperial College Schol.]

2.3. Comment on the value of including A and B elements in the same group of the Periodic Table. Refer in particular to the chemical characteristics of manganese and chlorine, or of chromium and sulphur. [Oxford Schol.]

2.4. " The valency of elements in the first row can usually be described by the octet rule." Give examples of the success and failure of this rule. Does the rule apply to the compounds of the second row elements? [Oxford Schol.]

2.5. The properties of the first member of a Group in the Periodic Table are often anomalous. Illustrate this by examples from the chemistry of fluorine, oxygen and nitrogen. [Oxford Schol.]

2.6. What do you understand by a " transition metal "? Describe with examples the characteristic properties of this type of metal, and explain how they can be accounted for. [Oxford Schol.]

2.7. The element Vanadium (V) occurs in the Periodic Table as indicated below:

			C	N	O	F
			Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn

Discuss the properties you would expect it to have. [Oxford Schol.]

2.8. The Periodic Table has been used to correct doubtful atomic weights and to predict the properties of elements before they were actually discovered. Give examples of these and other uses of the Table. What properties would you predict for element 85 (Astatine, symbol At) which now fills the space formerly vacant immediately below iodine? [Oxford Schol.]

CHAPTER 3

ATOMS AND ELECTRONS

Introduction

DALTON'S conception of an atom was a hard dense sphere. At that time it seemed impossible that any direct evidence for the existence of atoms could be obtained, much less that they could have a structure. In 1827, however, the botanist Robert Brown first observed the Brownian movement (expt. 3.1). He was examining pollen grains suspended in water with the newly invented achromatic microscope and he noticed that the grains had a small but continuous and erratic movement. He was quite unable to account for this and no explanation was produced until Wiener in 1861 suggested that it might be due to constant bombardment by the molecules of the water. Here was the first piece of direct evidence for the actual existence of molecules, but very little attention was paid to it at the time. The chemists and physicists of the nineteenth century were for the most part content to regard the atom as a convenient working hypothesis which explained the facts, but which was incapable of verification. Towards the end of the century, however, improvements in vacuum technique enabled considerable progress to be made in the study of the discharge of electricity through gases and this proved to be the key to the problem.

Gas discharges — the electron

When the terminals of an induction coil are connected to two platinum wires fused into the ends of a glass tube about 2 ft long and the coil operated, nothing happens. If the pressure in the tube is reduced a series of remarkable effects are observed. At a pressure of a few millimetres of mercury a thin bluish discharge passes along the tube. As the pressure falls the discharge spreads out and a dark space appears around the cathode. This is called the Faraday dark space. With a further fall in pressure striations appear in front of the Faraday dark space and constitute what is known as the positive column. The cathode meanwhile becomes surrounded with a bluish light known as the cathode glow. At about 10^{-2} mm a second dark space appears around the cathode. This is known as the Crookes dark space and as the pressure falls still further the cathode glow opens out, the positive column and Faraday dark space disappear through the positive end of the tube and the cathode glow fills the tube. Finally, the cathode glow disappears and all that can be observed is fluorescence of the glass walls of the tube.

If a metallic object is placed in the Crookes dark space it casts a shadow on the walls of the tube. A paddle-wheel is caused to rotate showing that whatever is coming from the cathode must be particulate as it can share its momentum with the wheel. Finally, if a metal plate with a hole in it is placed in front of the cathode and the end of the tube is coated with a fluorescent substance a bright spot of light can be seen. A magnet brought near to the outside of the tube causes this spot of light to move at right angles to the direction of the magnetic field. By applying the appropriate rule it is seen that the stream of particles coming from the cathode must be negatively charged. These particles are called " cathode rays ". Cathode rays are also deflected by an electric field but in this case the deflection is in the direction of the field. Again, the direction of deflection indicates a negative charge. These facts became known during the 1880's.

In 1895 Röntgen discovered that rays of a very penetrating nature were produced when cathode rays were allowed to fall on a metallic object. He called these penetrating rays X-rays. They were found to penetrate thick objects and to excite fluorescence in such substances as zinc sulphide and barium platinocyanide. They also produced a shadow of the bones of the hand on a fluorescent screen and this property was soon used in diagnostic medicine, particularly because X-rays could effect a photographic plate so that a photograph of a fractured limb could be obtained. The rays were undeflected by electric and magnetic fields and were soon identified as a form of electro-magnetic radiation similar to light waves but of very short wavelength.

Positive rays

In 1886 Goldstein, using a perforated cathode, noticed a bluish light appear behind the cathode provided the pressure in the tube was not too low. The rays coming through the cathode were called by Goldstein " canal rays ". Further investigators were able to show that these rays were deflected by a magnetic field, but in the opposite direction to cathode rays, showing that they were positively charged. They became known as positive rays and appear to originate in the Crookes dark space. Further reference will be made to them later.

The determination of e/m* for cathode rays

In 1897 Sir J. J. Thomson, working in the Cavendish Laboratory at Cambridge, devised an apparatus for measuring e/m. His reasoning was as follows: suppose the cathode rays were, in fact, a stream of electrically charged particles. If a magnetic field of strength B gauss be applied at right angles to this stream, the stream would be caused to move in a circle of radius r cm, following the normal laws of electro-dynamics (Fig. 3.1). If the charge on each particle is e (measured in e.m.u.) and the velocity v cm/sec, the force acting on the particle will be Bev dynes. Since the particle will move in a circle there will be an opposing centrifugal force $= mv^2/r$ dynes.

Hence
$$Bev = \frac{mv^2}{r} \tag{3.1}$$

and
$$\frac{e}{m} = \frac{v}{Br} \tag{3.2}$$

---

* The ratio of the charge to the mass.

The stream of particles could be made to fall on a fluorescent screen, B and r could be measured from the dimensions of the apparatus, the current and number of turns in the coil and the angle of deflection of the spot of light, but to determine v a second experiment would be necessary.

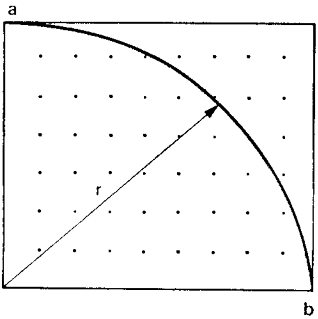


FIG. 3.1. Magnetic field acts perpendicular to the plane of the paper. The line *ab* shows the path of the cathode rays.

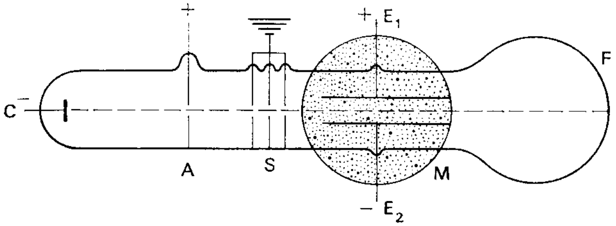


FIG. 3.2. C the cathode, A the perforated anode, S the series of earthed slits, E_1-E_2 the plates producing the electric field, M the coil producing the magnetic field, F the fluorescent screen. --- path of the rays.

As mentioned above, cathode rays can also be deflected by an electric field. Thomson accordingly constructed the apparatus shown in Fig. 3.2. The stream of particles from the cathode passed through a hole in the anode, and a series of slits was arranged behind the anode to produce a parallel beam which was rendered visible by allowing it to fall on a fluorescent screen of zinc sulphide on the end of the tube. The electric field acted at right angles to the magnetic field and its direction was so arranged that the spot of light was deflected exactly opposite to the deflection produced by the magnetic field. The magnetic field was first turned on and the angle of deflection of the spot of light recorded. Then the electric field was applied and adjusted until the spot of light was exactly returned to zero. If the strength of the electric field be X e.m.u. cm^{-1} then the force on the particle would be Xe dynes, due to the electric field and Bev dynes due to the magnetic field. For zero deflection,

$$Xe = Bev \tag{3.3}$$

therefore

$$v = \frac{X}{B} \tag{3.4}$$

and substituting in equation (3.2) for v gives

$$\frac{e}{m} = \frac{X}{B^2 r} \tag{3.5}$$

Thomson found that the value of v was about one-tenth of the velocity of light, but varied with the potential applied between cathode and anode, but e/m was constant and more important still was independent of the nature of the gas in the tube. He therefore concluded that these particles were constituents of all matter. He had discovered the electron — the atom of electricity. The value he obtained for e/m was approximately 10^7 absolute e.m.u./g.

An alternative method of measuring e/m for the electron uses a transverse magnetic field only, avoiding the application of the transverse electric field. If V is the voltage applied between anode and cathode (converted to e.m.u.), then

$$Ve = \tfrac{1}{2}mv^2 \tag{3.6}$$

Equation (3.1) can be rewritten

$$v = Br\frac{e}{m}$$

Squaring and substituting for v^2 from eqn. (3.6) gives

$$2V\frac{e}{m} = B^2r^2\frac{e^2}{m^2} \tag{3.7}$$

and

$$\frac{e}{m} = \frac{2V}{B^2r^2} \tag{3.8}$$

It is thus possible to obtain e/m in a single experiment by measuring V, B and r.

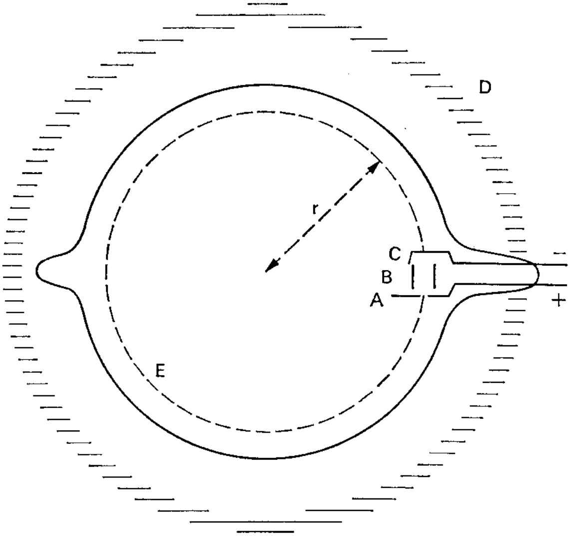


FIG. 3.3. The fine-beam tube. *A* perforated anode, *B* Wehneld cylinder, *C* cathode (heated independently), *D* Helmholtz coils, *E* path of electrons.

Several types of apparatus are now available for conducting this experiment. One of them, the fine beam tube, uses a beam of electrons surrounded with positive ions from a gas at low pressure (Fig. 3.3). The beam is rendered visible by luminescence from the positive ions. The spherical tube which contains the beam and electrode systems is placed between two Helmholtz coils which produce a more or less uniform magnetic field. The magnitude of the field strength B is determined from the current flowing in the coils. By suitably adjusting B the electron beam can be bent round in a circle. The radius r of this circle can be easily determined and knowing the voltage V applied to the tube, the three unknowns V, B and r of eqn. (3.8) can be determined.

The mass of the electron

Faraday had discovered that when 96,500 C of electricity were passed through a solution of dilute sulphuric acid, 1·008 g of hydrogen were liberated. Since the absolute electro-magnetic unit of charge is equal to 10 C this gives a value of e/m for the hydrogen ion of $9{\cdot}65 \times 10^3$ e.m.u./g. It follows from this that either the electron must carry a much larger charge than the hydrogen ion or if, as seemed probable, it carried the same charge, it must be very much lighter. To determine the mass of the electron it is necessary to know the charge e.

The charge on the electron

(i) TOWNSEND'S METHOD

The first experiments to determine e, the charge on the electron, were conducted by Townsend shortly after Thomson determined e/m. Townsend made use of the fact that gases produced in electrolysis carry a charge and when bubbled through water produce a cloud of water droplets. The total charge on the cloud was measured with an electrometer and the mass of the cloud determined by absorption with a drying agent. The radius of each drop was obtained by observing its rate of fall under gravity and applying Stokes' law ($v = 2gr^2\rho/9\eta$, where g is the acceleration due to gravity, r = radius of the drop, ρ = the density of the drop and η = viscosity of the medium). ρ is equal to unity since the drops were composed of water, η is the viscosity of the gas used and so r could be calculated. From the value of r, the mass of each drop and therefore the total number of drops could be found and hence the average charge carried. The value obtained by Townsend was 10^{-20} e.m.u. Comparing this with the value for e/m obtained by Thomson for the electron $= 10^7$ e.m.u./g gives a value for m, the mass of the electron, as 10^{-27} g — a very small quantity indeed.

(ii) MILLIKAN'S METHOD

As this is an example of one of the most careful and precise researches ever carried out it will be described in some detail. The work was conducted in the University of Chicago between the years 1909–16. Several papers were published during this time. Millikan first repeated Townsend's work and found that it suffered from a number of defects:

1. The charge carried by each drop of water was not constant.
2. The mass of the drops varied and consequently it was impossible to make accurate measurements of the rate of fall.
3. The water slowly evaporated and the rate of fall of any given drop was not constant.
4. Stokes' law was not strictly applicable to such small bodies.

Millikan eliminated these errors by using a non-volatile oil instead of water and by carrying out his observations on a single droplet rather than a cloud. He applied corrections to the simple form of Stokes' law by studying the behaviour of oil droplets of varying size.

The apparatus he used is shown diagramatically in Fig. 3.4. It was maintained at constant temperature by immersion in a thermostat (not shown). In addition it was possible to make measurements over a range of pressures. Droplets of oil blown by means of an atomiser A, using dust-free air, entered the chamber B. One or more passed through the pinhole p in the upper plate of the air condenser C. The pinhole could be closed by an electromagnetically operated shutter (not shown) to exclude the possibility of air currents in the condenser. The plates of this condenser were accurately machined and were held exactly 16 mm apart by means of three small ebonite posts (one shown at *D*). A strip of thin sheet ebonite with three glass windows, placed at angles of 0°, 165°, 180°, surrounded the plates forming a completely enclosed air space.

A narrow beam of light from an arc lamp *E*, filtered through water to absorb the heat, entered through the first window and emerged through the last. The third window was used to observe the motion of the oil droplet through a short-range telescope. The droplet appeared as a brilliant star against a black background. An electric field of between 3000 and 8000 V/cm could be produced between the plates by means of a battery of storage cells *F*. The exact potential between the plates was measured by means of an accurately calibrated electrostatic voltmeter. The plates could be short-circuited and the field destroyed by means of the switch *S*.

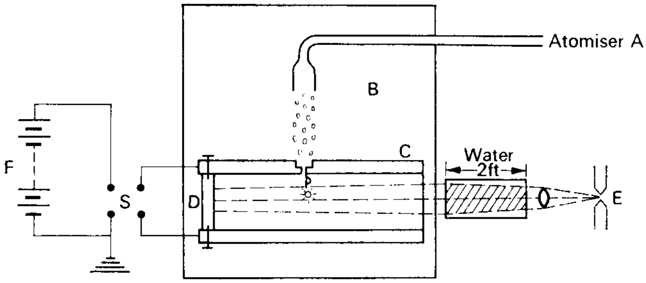


FIG. 3.4. Millikan's apparatus for determining the value of *e*, the charge on the electron.

The droplet which entered the condenser at *p* had received a frictional charge as it was blown out by the atomiser. If this charge was of the appropriate sign, the droplet could be pulled up by the field towards the upper plate, against gravity. Before it reached the upper plate the plates were short-circuited and the time the droplet took to fall under gravity a distance corresponding to the space between the cross-hairs of the observing telescope was accurately determined. Then the field was switched on and the upward movement of the droplet under the influence of the electric field was timed over the same distance. These operations were repeated a large number of times. Periodically the droplet captured an additional charge from an ion existing in the air, or a change of charge could be caused by passing a beam of γ-rays from radium through the chamber. The catching of this charge was signalled to the observer by an abrupt change of the speed of the droplet under the influence of the field. From the sign and the magnitude of these changes of speed, taken in conjunction with the constant speed under gravity the sign and the exact value of the captured charge could be determined.

Occasionally the droplet carried only one elementary charge and happened to capture a single charge of opposite sign. In this case the charge on the droplet was completely neutralised and it would start to fall under gravity unaffected by the electric field. This was a striking and direct visual proof of the atomic nature of the elementary electric charge.

The measurement of the distance corresponding to the space between the cross-hairs was made by means of a standard scale correct to 0·001 cm placed vertically at exactly the same distance from the telescope as the pinhole p. The timings were made with a calibrated chronograph, to 0·01 sec. If v_1 is the rate of fall under gravity in centimetres per second and v_2 the rate of upward movement under the action of the electric field, strength X e.s.u. opposed to gravity, e the electronic charge in e.s.u., n the number of charges carried by the drop and m the mass of the drop in grams, then

$$\frac{v_2}{v_1} = \frac{Xne-mg}{mg} \tag{3.9}$$

and

$$ne = \frac{mg}{Xv_1}(v_1+v_2). \tag{3.10}$$

m was obtained by using a modified form of Stokes' law (p. 37) applied to very small bodies. Some of Millikan's results are shown in Table 3.1.

The timings shown to two decimal places were made with a chronograph; the remainder with a stop-watch. The figures in column 3 were obtained by assuming the validity of Stokes' law to calculate the radius and hence the mass of the droplet from the known density of the oil. From Table 3.1 the mean value of e (weighted) = 5·143 × 10^{-10} e.s.u.

TABLE 3.1

1 Time of fall (sec)	2 Time of rise (sec)	3 Total charge on droplet ($ne \times 10^{10}$) (e.s.u.)	4 No. of charges carried	5 $e \times 10^{10}$ (e.s.u.)
24·61	151·9	25·75	5	5·150
24·4	152·9			
24·63	152·4			
24·6	153·5			
24·4	153·9			
24·7	39·4	36·03	7	5·147
24·8	39·2			
24·6	28·6	41·07	8	5·134
24·50	28·9			
24·59	29·0			
24·54	16·0	56·25	11	5·114
24·53	16·0			
—	15·8			

The above figures are typical of a long series of measurements. By applying corrections to Stokes' law Millikan eventually obtained the figure 4·774 × 10^{-10} e.s.u. — subsequent work has improved slightly on Millikan's figure by using a better value for η the viscosity of air, and the generally accepted figure for e the electronic charge is now 4·802 × 10^{-10} e.s.u.

The most recent value for e/m for the electron is 1·759 × 10^{7}

e.m.u./g. The value of e is

$$= \frac{4{\cdot}802 \times 10^{-10}}{2{\cdot}998 \times 10^{10}}*$$

$$= 1{\cdot}603 \times 10^{-20} \text{ e.m.u.}$$

and hence the value of m

$$= \frac{1{\cdot}603 \times 10^{-20}}{1{\cdot}759 \times 10^{7}} = 9{\cdot}107 \times 10^{-28} \text{ g}$$

(see expt. 3.2 for a simple method of carrying out Millikan's experiment in the laboratory).

Molecular and atomic radii

It was realised by the middle of the last century that an atom must be a very small body. Gold foils could be beaten to a thickness of about 4×10^{-5} cm at which point they became translucent, showing colours by interference. This gave an upper limit to the atomic radius. Very thin soap films show similar interference effects and just before the film breaks it is sometimes possible to see a black area which must be even thinner than the gold foil, of the order of 10^{-6} cm. Definite values for atomic radii were not obtained until the beginning of the present century. Most of the methods used are too complex for consideration here. Three will be discussed briefly.

(i) THE VAN DER WAALS EQUATION

A normal gas does not obey the simple gas law $PV = RT$, since the molecules exert attractions or repulsions on each other and occupy a definite fraction of the total space depending upon the temperature and pressure. Van der Waals derived an equation

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT,$$

---

* Electrostatic units of charge are converted to electromagnetic units by dividing by the velocity of light $2{\cdot}998 \times 10^{10}$ cm/sec.

which expresses the behaviour of most gases quite well except at very high pressures. a and b are not universal constants but each pair of values applies to a particular gas. The a/V^2 term represents the attraction between the molecules and will not be considered further here, but the b term is proportional to the volume occupied by the molecules and it can be shown that $b = 4Nv'$, where N represents the number of molecules in the volume and v' the volume occupied by each. N is clearly proportional to the Avogadro number (see p. 45). From a knowledge of b and N it is possible to calculate v', the volume occupied by each molecule. (The behaviour of gases is discussed in the volume *Physical Chemistry* of this series.)

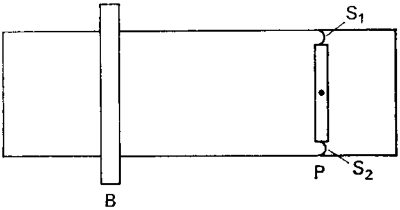


FIG. 3.5. Langmuir's trough. B is the movable barrier, P is the light paddle, S_1, S_2 light strips of platinum foil to prevent leakage of film past the paddle.

(ii) THE SPREADING OF OIL FILMS ON WATER

In the 1890's Lord Rayleigh and others had noticed that the area covered by a film of oil on the surface of water could be varied by confining the film between movable barriers and had suggested that it might be only one molecule thick. The first accurate measurements of film thicknesses were made by Langmuir in 1917. He dissolved a very small quantity of a fatty acid in a known volume of a volatile organic solvent such as benzene and allowed one drop of the solution to fall on a clean surface of water. The benzene evaporated and left a film of known weight. By means of a very light paddle floating on the water and attached to a lever to which small weights could be fixed, Langmuir was able to measure the force exerted by the film for different film areas (Fig. 3.5). The area was varied by moving a piece of wood coated with wax towards the paddle. He was thus able to plot force–area curves. The results are shown in Fig. 3.6. For large areas of film the force was very small, but on compression it increased at first slowly and then very rapidly. On reaching the point x the film crumpled and striations became visible. The value of the area corresponding to the point x was found to be $20{\cdot}5 \times 10^{-16}$ cm^2/molecule and was independent of the fatty acid used. Langmuir concluded that this was the cross-section of the hydrocarbon chain giving a radius of $2{\cdot}2 \times 10^{-8}$ cm, which must be somewhat greater than the radius of a carbon atom (see expt. 3.3).

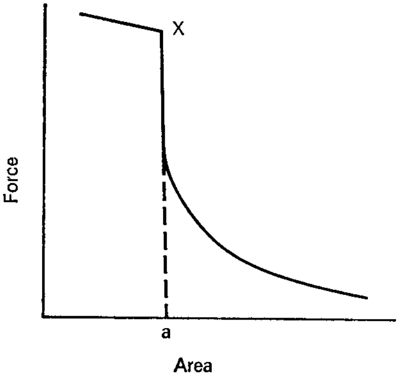


FIG. 3.6 Force–area curve. *a* represents the area of the film when the molecules are in contact.

(iii) X-RAY DIFFRACTION

When a narrow slit is illuminated by monochromatic light and an image of the slit is allowed to fall on a glass surface on which a number of very fine lines have been ruled, diffraction images of the slit can be observed with the aid of a telescope. If the wavelength λ of the light is known and the angle of diffraction θ can be measured, the distance d between the lines can be calculated from the relationship $n\lambda = 2d \sin \theta$ where n is an integer. For the first diffraction image $n = 1$. (For further information on this point the student is referred to a textbook of physics.) X-rays can be similarly diffracted by a crystal, and in this case the lines are represented by the arrangement of the ions in rows in the crystal lattice, and the diffraction images are caused by reflection of the X-rays from successive planes in the crystal. A crystal of sodium chloride which has a cubic lattice, is very suitable for use as an X-ray diffraction grating. The distance d separating each layer of ions in the crystal can be determined provided the wavelength λ of the X-rays is known. (For the measurement of d see Appendix 2, p. 135.)

At first sight it would seem to be impossible to determine λ for X-rays with a mechanically ruled diffraction grating since the value of λ is so much smaller than for visible light. A consideration of the above equation, however, will show that it is not impossible. If λ is much smaller than d then θ must be made correspondingly small. Compton and Dean in 1925, making use of the fact that the refractive index of metals for X-rays is less than unity, obtained total reflection at a ruled metal diffraction grating at a glancing angle of 30′. They obtained diffraction bands and were able to measure the wavelengths of the X-rays. Hence, by applying the equation

$$d = \frac{n\lambda}{2 \sin \theta} \tag{3.11}$$

and assuming that the ions are in contact, the distance d between the centres will be twice the mean of the ionic radii.

The Avogadro number

This quantity refers to the number of molecules in 1 gram molecule of a substance and is of great theoretical interest. No accurate determinations were made until the beginning of the present century.

(i) THE METHOD OF RUTHERFORD AND GEIGER

This depends on the radioactive decay of radium. Radioactivity is treated in detail in *Nuclear and Radio Chemistry*; it is sufficient for our present purpose to know that a radium atom decays by emission of an α-particle, which is a helium atom carrying two positive charges, and in the process is converted to an atom of the rare gas radon. This in turn emits an α-particle and becomes an isotope of polonium. The polonium in its turn decays further and the process stops at the formation of lead. If the number of α-particles emitted in a given time by a given mass of radium in equilibrium with its decay products could be counted and the volume of helium formed in the same time could be measured, this would give the number of atoms of helium (molecules since helium is monatomic) contained in the given volume, and by proportion the number of molecules in 22·4 l, i.e. the Avogadro number.

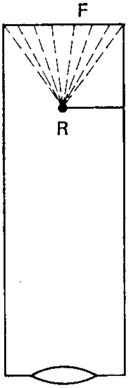


FIG. 3.7. The spinthariscope. *R* is the speck of radium. *F* is the fluorescent screen.

The problem of counting α-particles was a difficult matter in 1908 since electronics was still in its infancy. Sir William Crookes had invented the spinthariscope in 1902. This beautiful little instrument consisted of a tube fitted with a lens at one end and a fluorescent zinc sulphide screen at the other. A tiny speck of radium was placed in front of the screen and little flashes were seen through the lens where the α-particles struck the screen (Fig. 3.7). Even a microgram of pure radium emits $3{\cdot}7 \times 10^4$ α-particles per second and in the presence of its decay products five times this number will be emitted so that in order to count the α-particles visually it was necessary to use a very small solid angle and only count a fraction of the α-particles emitted by the piece of radium. Rutherford obtained an approximate value for the number of α-particles emitted by a given mass of radium in a given time by visual counting, but the method was liable to error because of imperfections in the fluorescent screen, which meant that some of the α-particles might not produce a flash at all and so be missed. Rutherford and Geiger improved on this method by inventing an ionisation chamber and so counting the α-particles electrically. Their apparatus is shown in Fig. 3.8. Their counter consisted of a narrow brass tube containing carbon dioxide at 40 mm pressure, with a central insulated wire. The central wire was connected through an electrometer to the positive pole of a high voltage supply, the negative pole being connected to the outside of the brass tube. The glass tube D which led into the brass tube, ended in a fine capillary, diameter 1·5 mm and this was sealed with a very thin sheet of mica through which α-particles

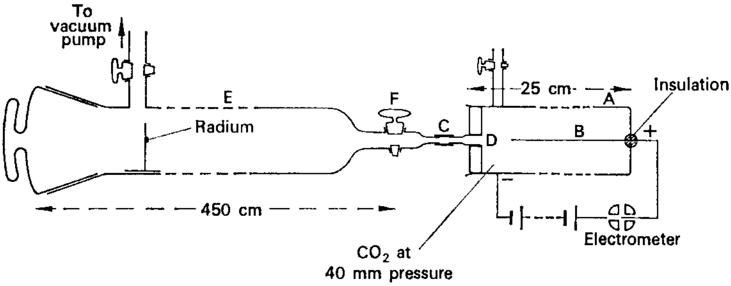


FIG. 3.8. Apparatus of Rutherford and Geiger for counting α-particles, electrically.

could pass. Connection with the tube *E* was made with a piece of thick-walled rubber tubing. The radium compound in the form of a thin film on a metal plate covered with a thin sheet of mica was placed in the tube *E* at a known distance from the hole in the end of the tube *D*. The mass of radium used was 55·8 μg and was determined by comparing its activity to the activity of a known mass of radium. The stopcock *F* was closed and the tube *E* exhausted to a high vacuum. The voltage between the wire *B* and the outer brass tube *A* was adjusted until it was just below the sparking potential and then the stopcock *F* was opened. α-particles entered the tube *A* through the sheet of mica at the rate of 4 or 5 per minute. Each α-particle produced a number of positive ions by collision with the gas molecules in the tube. The resulting electrons set free were accelerated towards the wire *B* and in the process liberated more electrons by collision with the gas molecules. The result was to produce an appreciable charge on the central wire, which then discharged through the electrometer producing a sudden ballistic throw. Here was the first use of the principle of gas amplification which has been developed into the modern Geiger counter. The rate of counting was very slow as it took several seconds for the ions formed to be all discharged. Prolonged periods of counting were necessary.

Let the number of α-particles entering the tube *A* per hour be x. Let the area of the small hole in *D* be a and let the distance of *D* from the radium source be r. Then the number of α-particles emitted by the source in all directions per hour will be

$$n = \frac{4\pi r^2 x}{a} \tag{3.12}$$

Taking the value of x at 240 (a typical value), $r = 400$ cm and $a = 0{\cdot}0177\ \text{cm}^2$, gives

$$n = \frac{4\pi \times 400^2 \times 240}{0{\cdot}0177}$$

$= 2{\cdot}73 \times 10^{10}$ for 55·8 μg of radium/hr. This is equivalent to $4{\cdot}9 \times 10^{14}$ α-particles emitted per gram of radium/hr.

Rutherford and Boltwood determined the volume of helium given out by a known mass of radium in a given time by placing 192 mg of radium as radium chloride contained in a thin platinum capsule in a glass tube which was then exhausted. After 83 days the tube was heated strongly to drive off all the helium. The helium was collected, purified and its volume measured. They obtained $6{\cdot}58 \times 10^{-3}$ c.c. of helium at N.T.P. Such a small volume had to be measured by means of a Macleod gauge at low pressure. Hence the volume of helium given off per hour per gram of radium in equilibrium with its decay products

$$= \frac{6{\cdot}58 \times 10^{-3}}{0{\cdot}192 \times 83 \times 24} = 1{\cdot}72 \times 10^{-5} \text{ c.c./hr.}$$

This is the volume of helium containing $4{\cdot}9 \times 10^{14}$ atoms (molecules of helium), therefore 22,400 c.c. of helium contain

$$\frac{4{\cdot}9 \times 10^{14} \times 22{,}400}{1{\cdot}72 \times 10^{-5}}$$

$$= 6{\cdot}38 \times 10^{23} \text{ molecules}$$

Considering the extreme difficulties of measuring the very small quantities involved with the techniques then available this is a remarkably accurate figure.

(ii) PERRIN'S METHOD

This research was carried out in 1908 and was based on a study of the Brownian movement of colloidal particles. When such particles are suspended in a liquid they distribute themselves in the same way as gas molecules in an atmosphere, being in equilibrium under the force of gravity acting down and the Brownian movement acting in all directions. Just as the number of gas molecules per cubic centimetre decreases with height in geometrical progression, so the number of colloidal particles per cubic centimetre decrease with height in the same way, but as they are much more massive than gas molecules the settling produced by gravity is much greater and the " height of the atmosphere " correspondingly smaller. With the size of particle used by Perrin a rise of $\frac{1}{20}$ mm halved the number of particles per cubic centimetre.

The colloidal particles behave like large molecules and possess the same mean kinetic energy as the molecules of the liquid. Perrin deduced the following equation:

$$\frac{2}{3}E\log_e\frac{n_0}{n} = v(D-d)gh, \tag{3.13}$$

where E is the mean kinetic energy of the particles, n_0 and n are the average number of particles per cubic centimetre at levels differing in height by h; v is the volume of the particle; D and d are the densities of the particles and the liquid respectively.

From the kinetic theory of gases (see the volume *Physical Chemistry* of this series) it can be shown that for 1 mole of a perfect gas at constant temperature,

$$PV = \tfrac{1}{3}Nm\overline{u^2},$$

where P is the pressure in dynes per square centimetre, V the volume occupied by 1 mole in cubic centimetres, N is Avogadro's number, m the mass of a molecule in grams, $\bar{u}$ the root mean square velocity in centimetres per second. The mean kinetic energy of the molecule is $\frac{1}{2}m\overline{u^2}$. Hence, from the above equation,

$$\tfrac{1}{2}m\overline{u^2} = \frac{3PV}{2N} = \frac{3RT}{2N} \tag{3.14}$$

Assuming this theory holds for liquids $\frac{1}{2}m\overline{u^2}$ will be equal to E, the mean kinetic energy of the colloidal particles. Substituting for E in the first equation and rearranging terms gives

$$N = \frac{RT}{vgh(D-d)}\log_e\frac{n_0}{n} \tag{3.15}$$

Perrin used colloidal solutions of gamboge and mastic in water. The solutions were made by dissolving the substances in alcohol and then adding water to produce the colloidal solution. Particles of uniform size were obtained by repeated centrifuging.

The diameter and hence the volume of the particles was determined by evaporating a small drop of the colloidal solution on a microscope slide. The particles ran together and arranged themselves in rows. The length of a row was measured under the microscope and the number in the rows counted, thus giving the diameter of each particle. Other methods were used and they gave sensibly the same result. A typical value for the diameter of the particles used by Perrin in one set of measurements was $0{\cdot}5\mu$ (i.e. 5×10^{-4} mm). The mass of each particle was determined by weighing a known number, obtained by direct counting through the microscope. The mass and diameter being known, the values of v and D could be determined.

The numbers n_0 and n were determined by counting the number of particles in two layers of the solution separated by a height h. This was a very difficult matter as the particles were continually moving in and out of the field of view. Perrin overcame the difficulty in a most ingenious way. He placed a disc of foil with a small hole pierced by a needle in the focal plane of the microscope. In this restricted view he was able to determine at once the number of particles to be seen at any given moment. He placed a shutter in the path of the rays and made a large number of observations at regular intervals. Owing to the irregularity of the Brownian movement 100 observations of this kind were equivalent to a single observation over 100 times the area.

Perrin had now determined all the unknowns in his final equation and was so able to calculate N. He repeated his measurements for particles of different sizes suspended in solvents of different density and viscosity. In spite of all these variations the value of N remained between the limits of $6{\cdot}5$ and $7{\cdot}2 \times 10^{23}$ which agreed closely with the value obtained by Rutherford.

(iii) MILLIKAN'S METHOD

The determination of e, the electronic charge (see p. 37) enables N to be calculated from the Faraday — the charge carried by 1 mole of hydrogen ions. The Faraday can also be defined as the charge carried by 1 mole of electrons. The value of the Faraday is

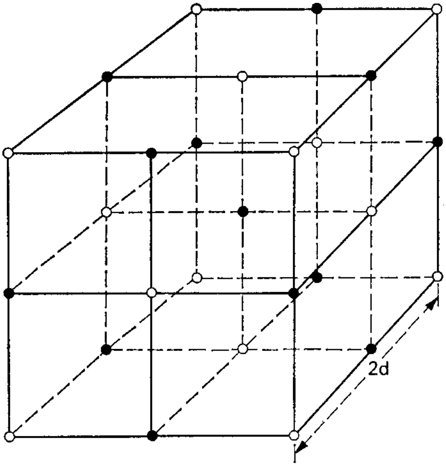
9649 absolute e.m.u. Hence

$$N = \frac{9649}{1{\cdot}603 \times 10^{-20}} = 6{\cdot}023 \times 10^{23}$$

This is probably the most accurate determination of N.

(iv) METHOD USING LATTICE SPACINGS

The measurement of the distance separating the layers of ions in a crystal may also be used to determine the Avogadro number.



○ = Sodium ions.
● = Chloride ions

FIG. 3.9. Crystal of sodium chloride.

Consider a crystal of sodium chloride represented by Fig. 3.9. Each of the eight sodium ions at the corners must form part of eight similar cubes in the crystal. Similarly, the six sodium ions in the centre of each face must each form part of two similar cubes. Thus each complete cube as represented in the diagram may be regarded as a unit cell containing four sodium ions. If the chloride ions are considered it will be seen that the one in the centre must belong exclusively to this cell, but the other twelve will be shared equally between four adjacent similar cells. It will thus be seen that there are also four chloride ions in the unit cell.

Now the length of each edge is $2d$, where d is the lattice spacing. The volume of the unit cell is therefore $8d^3$. The mass of the four sodium and four chloride ions is $4M/N$ where M is the formula weight of sodium chloride and N is the Avogadro number. Let ρ be the density of sodium chloride. Then

$$\frac{4M}{N\rho} = 8d^3$$

or

$$N = \frac{M}{2d^3\rho} \tag{3.16}$$

Since d can be determined by X-ray diffraction to a high degree of precision, this gives another and very accurate method for determining N.

The Avogadro number has now been determined by several different methods and they agree within the limits of experimental error though the methods of Perrin, and Rutherford and Geiger are less accurate than the others. The determination of this number has proved that the atom postulated by Dalton is a real particle with a physical existence; it has proved the truth of Avogadro's hypothesis which as applied to a perfect gas must be regarded as a fact; it has put Cannizaro's theory for the determination of atomic weights on a sound physical basis; it has enabled the actual masses of individual atoms and molecules to be determined. The determination of this number was therefore of fundamental importance to chemistry. The figure in use today is $6{\cdot}023 \times 10^{23}$.

EXPERIMENTS

3.1. TO VIEW THE BROWNIAN MOVEMENT

Place a drop of Aquadag (colloidal graphite) in a test tube and dilute with about 1 ml of water. Withdraw a drop of the diluted solution, place on a microscope slide and view with an oil-immersion objective.

An alternative method is to view a solution of colloidal gold with a dark ground condenser and an intense source of light such as the sun. A particularly fine view of the Brownian movement can be obtained with a $\frac{1}{6}$ in. objective and a × 10 or × 15 eyepiece. Colloidal gold can be easily prepared by adding 1 ml of a 1 % or 2 % gold chloride solution to 100 ml of conductivity water containing about 4 ml of M/20 potassium carbonate solution, heating to boiling and adding 2 ml of 0·4 % formalin. It is essential to use an absolutely clean beaker made of resistance glass. The solution should be a clear ruby red by transmitted light. It should be stored in a flask made of resistance glass fitted with a cork covered with tinfoil.

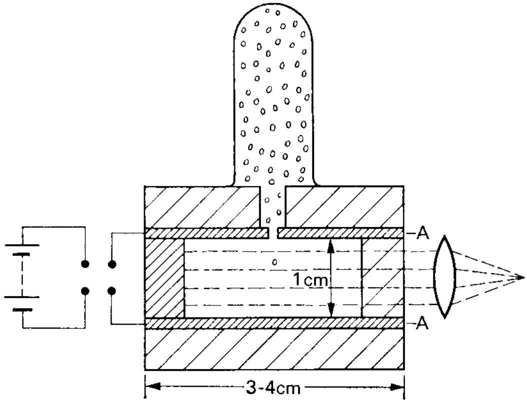


FIG. 3.10. Simple Millikan cell.

3.2. MILLIKAN'S EXPERIMENT

A small cell is constructed with three sides made of glass. The top and bottom should be thick to form good insulation. Suitable dimensions are given in Fig. 3.10. The plates *AA* are of brass covered with a 0·5 cm layer of plastic and the remaining two side walls should also be made of an opaque plastic. A 1 mm hole should be made in the upper brass plate and a slightly larger hole in the upper piece of plastic.

The brass plates are charged with a suitable d.c. supply to a known potential of 200–300 V. A parallel beam of light is arranged to enter through one of the transparent sides and a travelling microscope with an eyepiece fitted with a micrometer scale is focused on the centre of the cell through the second transparent side. An atomiser, obtainable at most chemists, is used to blow fine drops of a suitable non-volatile oil into a boiling tube. The coarse drops are allowed to settle and the tube is then inverted over the centre of the hole in the upper brass plate. A few fine droplets will find their way into the cell and can be viewed with the travelling microscope. The droplets should become charged by friction.

The field is switched off, one of the drops is observed and its rate of fall measured under gravity. By applying Stokes' law

$$\left(v = \frac{2}{9}\frac{gr^2\rho}{\eta}\right)$$

the radius and hence the mass of the drop is determined (p. 37). The field is then switched on and the rate of upward movement determined (it may be necessary to reverse the direction of the field). By applying the equation on page 40 it is possible to determine the charge on the electron. It is important to insulate the apparatus from shocks and the cell should be standing on a piece of thick rubber. (The design and construction of this cell is the work of Rev. J. L. Birley.)

3.3. MEASUREMENT OF THE CROSS-SECTION OF THE OLEIC ACID MOLECULE

A suitable apparatus for conducting this experiment is illustrated in Fig. 3.11. The trough and the vertical portion are made from $\frac{1}{8}$ in. perspex. The dimensions are given in the figure, but they are not critical. The trough rests on four levelling screws. It is important to grind the upper edges of the sides flat so that the perspex barriers *AA* fit them closely. The float *B* can be made of aluminium or thin copper and should be 1–2 cm shorter than the width of the trough. Very light strips of polythene are attached to the ends of the float and rest against the sides of the trough. These are to prevent the surface film from leaking past the float which is attached at *D* to the light aluminium strut *C*. It is essential that *C* should be the correct length so that the float rests on the surface when the trough is filled to the brim. *C* is connected to a small brass collar with a set screw, and a light rod *E* is also attached to the brass collar and projects to the back of the trough at 90° to *C*, ending in a hook. It is convenient to make *C* and *E* in one piece. A thin copper wire is fixed at *GG* and stretched fairly taut with a clamping screw. This wire carries a small mirror which consists of a microscope cover slip silvered on one side and secured to a thin piece of copper as support. The copper support has two lugs which slide on the wire and two light copper tails which serve to balance the mirror. The support is attached to the vertical rod *C* by a small piece of thread. The object of the mirror is to form an optical lever. The upper torsion wire *F* is made of phosphor bronze 0·2 mm diameter. The wire is

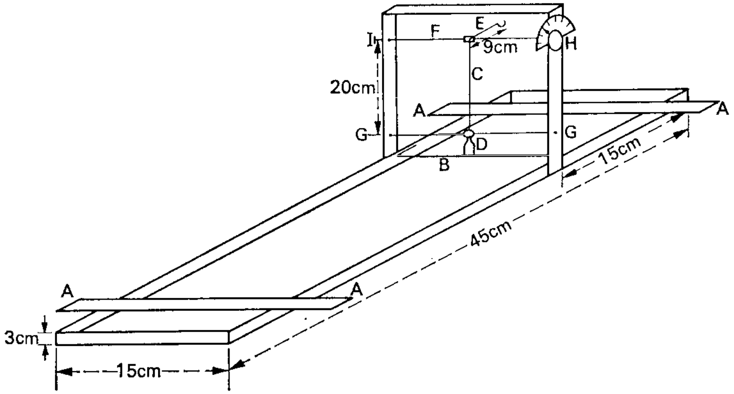


FIG. 3.11. Langmuir trough.

attached to *H* by a suitable clamping screw such as a " collet ", and can be stretched taut by means of the brass screw *I*. Torsion can be applied by rotating the circular knob *H*. A pointer is fitted to *H* and moves over a scale divided into degrees.

When using the apparatus the trough must be thoroughly cleaned and then filled to the brim with clean water or dilute acid, depending on the experiment. The surface must be scraped several times with the barrier *AA* in a direction away from the float to remove any surface contamination. A lamp and scale, such as is used for mirror galvanometers, is arranged with the scale vertical so that the mirror reflects a spot of light on to the scale. A 10 mg rider is suspended from the hook *E* and the torsion wire *F* adjusted by turning the knob *H* until the spot of light returns to its original position. From the dimensions of the apparatus the force in dynes equivalent to the weight of the rider which would act horizontally on *B* can now be calculated and expressed in dynes per centimetre. Allow half the width of the gaps blocked by the polythene strips as belonging to the float. The scale *I* can now be calibrated in terms of dynes per centimetre length of the float.

Prepare a solution of oleic acid or other suitable organic acid by dissolving about 0·05 g weighed accurately in 100 ml of ether. Prepare a solution of hydrochloric acid about 0·01 M sufficient to fill the trough. About 2 l. will be required. Pour this into the trough. Scrape the surface several times on both sides of the float using the movable barriers *AA*, and then measure the surface pressure developed on moving the forward barrier towards the float so that the area between the float and the barrier is reduced to one-quarter. A very clean surface will develop a pressure of less than 0·03 dyne/cm, but if the pressure does not exceed 0·1 dyne/cm the surface is sufficiently clean for this experiment. Return the barriers to the end of the trough and observe the position of the spot of light on the scale. Apply the film by allowing 0·1 ml of the oleic acid solution to fall on to the surface. The ether will evaporate rapidly and leave a film of oleic acid. Rotate the knob *H* until the spot of light returns to its original position and calculate the surface pressure developed. It will be very small. Compress the film gradually and plot a surface pressure (force)/area curve. When the area has been reduced to about half, the pressure should start to rise and it should rise very steeply when the area is reduced to about 200 cm^2. These figures apply to the concentration of oleic acid recommended. Produce the steep portion of the curve backwards and read the value where it cuts the abscissa, which corresponds to the area. From the weight of oleic acid taken, calculate the cross-sectional area of the oleic acid molecule.

A number of other experiments can be done with this trough. For further work a book on surface chemistry should be consulted.

QUESTIONS

3.1. Determine the charge on the electron in e.s.u. from the following data: the Faraday = 96,500 C, the Avogadro number = $6{\cdot}023 \times 10^{23}$, the velocity of light = $2{\cdot}99 \times 10^{10}$ cm/sec.

3.2. Discuss the effect of the discovery of the electron on the subsequent development of chemistry. [Oxford Schol.]

3.3. A parallel beam of electrons, accelerated through a potential difference of 1000 volts, is injected horizontally half-way between two horizontal conducting plates 4 cm apart charged to a difference of potential of 100 volts. Find the horizontal distance from the point of injection to the point of impact of the electrons on one of the plates.

Describe in general terms the effect on the beam of a horizontal magnetic field at right angles to the beam.

Find the value of such a field if the path of the beam remains horizontal.

(e/m = $5{\cdot}31 \times 10^{17}$ e.s.u./g; 1 e.s.u. = 300 volts; velocity of light = 3×10^{10} cm/sec). [Oxford Schol.]

3.4. An electron falls through a potential difference of 10 volts in a vacuum. Calculate its velocity. (e/m for an electron = $5{\cdot}27 \times 10^{17}$ e.s.u. gm^{-1}) [Cambridge Schol.]

3.5. Explain how the velocity and the ratio of charge to mass of atomic or sub-atomic particles can be measured. Describe what you consider to be a practicable arrangement for measuring these quantities for an electron, estimating, as far as you can, the magnitudes involved (e.g. the field strengths).

A proton has a velocity of 4×10^9 cm sec^{-1}, a charge (e) of 5×10^{-10} e.s.u. and a mass of 2×10^{-24} gm. It moves in a circular orbit in a uniform magnetic field of strength 10,000 gauss. What is the radius of the orbit? For a proton of this velocity how could the radius be substantially reduced? [Cambridge Schol.]

3.6. Discuss briefly the importance of the rare gases in the development of chemical ideas. The density of solid argon is 1·65 gm/ml. Derive a rough value for Avogadro's number, taking the atomic weight of argon to be 40, and the diameter of an argon atom to be $3{\cdot}2 \times 10^{-8}$ cm. [Oxford Schol.]

3.7. Sixty years ago the electron was discovered. Outline the importance of this discovery in the development of chemical theory, especially with regard to the basis of the modern system of classification of the elements and to ideas of valency. [Imperial College Schol.]

3.8. The following figures are obtained from measurements made by Millikan. Distance corresponding to the space between the cross-hairs = 0·522 cm. Mean time of fall of the droplet under gravity = 13·595 sec. Times in seconds of successive upward movements of the droplet under the influence of the electric field: 12·45, 21·85, 34·70, 84·50, 16·00. What are the probable values for n, the number of charges carried by the droplet, on each occasion?

3.9. In Millikan's oil-drop experiment the drops are observed to move (under the action of constant forces due to gravity and any uniform electric field that may be present) with constant velocity. Explain why their velocity, rather than their acceleration, is constant.

In this experiment an oil-drop was prevented from falling or rising by applying a potential difference of 5750 volts between parallel horizontal plates 1·5 cm apart. Assuming that the drops each carried one electron charge ($1{\cdot}60 \times 10^{-19}$ coulomb) what was the radius of the drop?

(Density of oil = 0·92 gm cm^{-3}
1 volt = 1/300 e.s.u. of potential
1 coulomb = 3×10^9 e.s.u. of charge
g = 981 cm sec^{-2}).

[O. & C. G.C.E.]

CHAPTER 4

ATOMIC STRUCTURE

Introduction

IN THE last chapter it was shown that the determination of the Avogadro number enabled the actual masses of atoms and molecules to be determined. The mass of a single hydrogen atom is $1{\cdot}673 \times 10^{-24}$ g and a single carbon atom is $2{\cdot}007 \times 10^{-23}$ g. Both these figures refer to the light isotopes (p. 6) of these elements. The diameter of a carbon atom is about 1×10^{-8} cm. The evidence for the structure of such small bodies will now be considered.

The discovery of the electron by Sir J. J. Thomson in 1897 and his proof that it was a constituent of all matter led him in 1904 to a suggestion for the internal structure of atoms. He postulated that the atom was a uniform sphere of positive electrification with negatively charged corpuscles (electrons) circulating in orbits within the sphere, the number in each orbit increasing on moving outwards from the centre.

Thomson drew a parallel between his model of the atom and Mendele'ef's periodic table. He showed mathematically that certain combinations of electrons in an outer ring would be unstable. A ring with too few would tend to gain electrons and form negative ions and one with too many would tend to lose electrons and form positive ions. This would account for the electro-negative elements at the end of a period, followed by the noble gases with a stable ring, and the electro-positive elements at the start. The theory was the first attempt to correlate the chemical properties of the elements with the structure of their atoms. It was a great step forward, but unfortunately it ran into difficulties, the chief of which was that the mass of the atom was supposed to be equal to the sum of the masses of the electrons it contained, the positive electrification having no mass. Since the mass of the electron was soon shown to be 1/1800 of the mass of the hydrogen atom, a hydrogen atom would have to contain 1800 electrons. This seemed improbable.

The nuclear atom

Rutherford's theory of the nuclear atom, which was put forward in 1911 to explain the scattering of α-particles by metal foils, is in its essentials similar to that in use today. The experimental work which led to the theory was conducted by Geiger and Marsden, two of Rutherford's research students. The apparatus which they used is shown in Fig. 4.1a. The α-particles were observed by the scintillations they produced on a fluorescent screen. A small but intense source of α-rays was placed at *A* and a narrow pencil of homogeneous rays was obtained by means of the slit *B*. The apparatus was evacuated and the rays allowed to fall on a fluorescent zinc sulphide screen at *C*. A bright band of light was observed on the screen. Pieces of thin metal foil were then introduced at *D* and the bright band vanished due to scattering of the α-particles over a much greater area. Observations on the distribution of the α-particles over a given area at different distances from the screen were made by counting the scintillations with the aid of a microscope. The degree of scattering depended upon the thickness of the foil and the atomic weight of the metal.

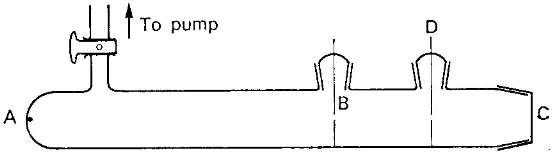


FIG. 4.1(a). Geiger's apparatus to measure the scattering of α-particles by gold foil.

Though most of the α-particles emerged on the opposite side of the foil a very small fraction of them was scattered through such large angles that they emerged again on the side of incidence. The amount of this diffuse reflection increased, at first, with increasing thickness of the foil, showing that it was a volume and not a surface effect. With the source used, 1 in 8000 α-particles incident on a gold foil was scattered through 90° or more. (Figure 4.1b illustrates the effects observed.)

To account for these results Rutherford supposed that the deflections were caused by encounters with a relatively heavy positively charged body and from the proportion of the deflections exceeding 90° he was able to show mathematically that the body must be very small, of the order of 10^{-12} cm diameter. As the diameter of the atom was known to be of the order of 10^{-8} cm, this meant that the mass of the atom must be concentrated in a nucleus. By assuming that this nucleus was effectively a point charge, Rutherford was able to apply Coulomb's inverse square law to the interaction of the α-particle with the nucleus. He showed that the path of the α-particle would be a hyperbola with

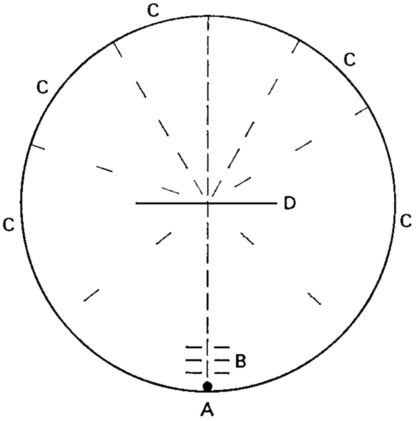


FIG. 4.1(b). To illustrate the observed scattering. *A*, source of α-particles; *B*, slits; *C*, fluorescent screen; *D*, metal foil.

the charged nucleus at the external focus (Fig. 4.2) and he deduced an equation to account for the proportion of α-particles scattered through a given angle. The scattering experiments were continued by Marsden and verified Rutherford's equation conclusively. The results indicated that the charge on the nucleus was approximately equal to half the atomic weight of the atom. Rutherford therefore concluded that the atom must consist of a positively charged nucleus surrounded by electrons to maintain electrical neutrality.

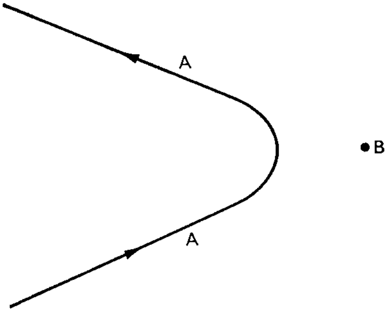


FIG. 4.2. *A* the path of the α-particle. *B* the charged nucleus.

Spectra

X-RAY SPECTRA

Striking evidence in support of Rutherford's theory of atomic structure was obtained 2 years later as a result of the work of Moseley. Moseley was one of the most brilliant young scientists of his time. He came from a distinguished family, for his two grandfathers and his father were Fellows of the Royal Society. He was educated at Eton and Trinity College, Oxford, and, after graduating, joined Rutherford at Manchester as a lecturer. Rutherford said of Moseley that he was " one of those rare examples of a man who was a born investigator ". Moseley soon decided to devote his whole time to research and, resigning his lectureship, began a study of the X-ray spectra of the elements.

X-rays are produced when cathode rays, i.e. high energy electrons, are caused to fall on matter in a discharge tube at very low pressure. The object on which they fall is called the anti-cathode and is connected electrically to the anode which is situated in the side of the tube (Fig. 4.3). X-rays are a form of electro-magnetic radiation similar to light, but of much shorter wave length (higher frequency). They are able to excite fluorescence in certain substances, they will affect a photographic plate wrapped in black paper and can even penetrate thin sheets of metal, the degree of penetration increasing with the frequency. In 1913 Moseley returned to Oxford and it was there that he wrote the second of his two famous papers. In the summer of 1914 he was attending a conference in Melbourne when the Great War broke out. He returned to England, volunteered for the army, was commissioned as a signals officer and was killed at Gallipoli in 1915.

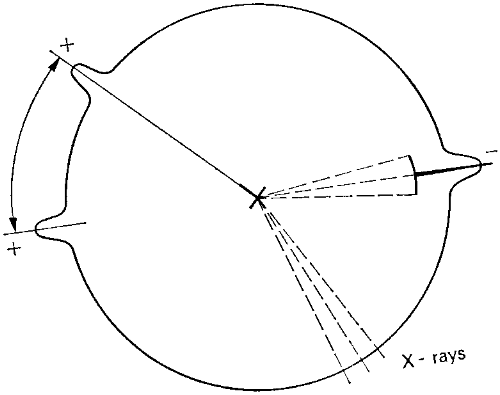


FIG. 4.3. An X-ray tube.

The apparatus which he used for his study of X-ray spectra (Plate 4.1) was constructed with remarkable ingenuity. A series of elements were placed on a trolley in the evacuated tube, which was moved by means of the ground joints *AA* attached to the trolley with fishing line. Each element in turn was made the anti-cathode

PLATE 4.1. H. G. J. Moseley's X-ray spectrograph, from experiments with which it became clear that the atomic number of an element is numerically equal to the positive charge on the nucleus.

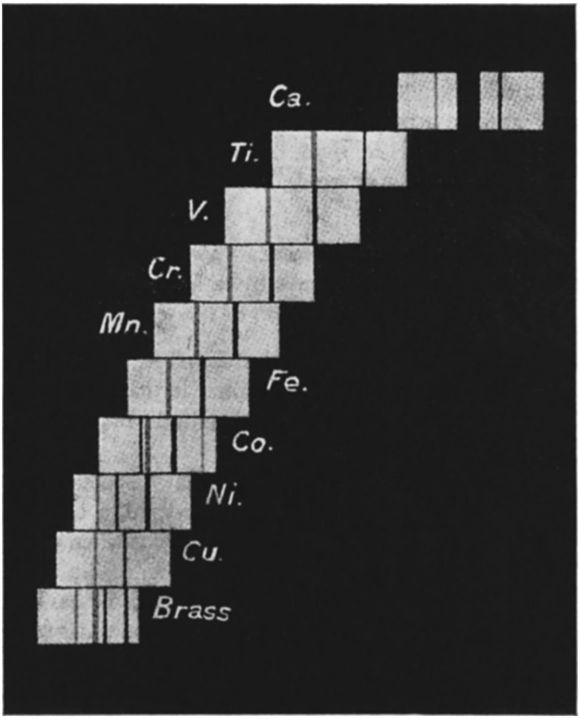


FIG. 4.4. X-ray spectra to show missing element scandium.

in the X-ray tube. Moseley constructed a simple X-ray spectrometer using a crystal of potassium ferrocyanide as a diffraction grating. The X-rays produced by the element were passed through a narrow slit on to the crystal, and the diffraction spectrum recorded on a photographic plate.

X-ray spectra are much simpler than optical spectra. For the light elements, up to and including neon the spectrum consists of one group of lines only called the K series. The heavier elements show additional groups called the L, M and N series which are of longer wavelength than the K series. The X-rays of the K series are more penetrating than those of the L series and the degree of penetration of both increases with increasing atomic weight of the element. In each series one particular line called the K_α, L_α, etc., is much brighter than the rest.

Moseley measured the angle of diffraction θ for the K_α line in the spectrum of each element. He knew the lattice spacing in potassium ferrocyanide and by use of the equation $n\lambda = 2d \sin\theta$, where d is the lattice spacing, λ the wavelength and n an integer, he was able to calculate λ and hence the frequency ν.* The value of n depends on the order of the spectrum. For the first order spectrum $n = 1$.

Moseley found that if he plotted the square root of the frequency of the K_α lines against the atomic number, i.e. the position of the element in the periodic table, he obtained a straight line graph. His equation can be expressed as follows:

$$\sqrt{\nu} = a(Z-b) \tag{4.1}$$

where ν is the frequency, Z the atomic number and a and b are constants. a is a simple proportionality constant and b is constant for all the lines of a given series. No such simple relationship exists between the frequency and the atomic weight. Figure 4.4 shows the spectra of a typical series of elements. It is clear that an element is missing between calcium and titanium.

Moseley's work showed with exceptional clarity the significance

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* $\nu = c/\lambda$ where c is the velocity of light $2{\cdot}99 \times 10^{10}$ cm sec^{-1} and λ is the wavelength in centimetres.

of atomic number. He concluded that this quantity was fundamental for each element and was in fact equal to the positive charge on the nucleus. In addition, he was able to show that argon and potassium; cobalt and nickel; tellurium and iodine were correctly placed in the periodic table, despite the fact that they were not in the order of their atomic weights. Finally, he was able to show that there could be only fourteen rare earth elements and that element No. 72 (hafnium) was missing. His work proved beyond question that only 92 elements could exist between hydrogen and uranium inclusive and he was able to restate the periodic law as " the properties of the elements are periodic functions of their atomic numbers ".

OPTICAL SPECTRA

When a solid is heated to incandescence it emits a more or less continuous optical spectrum, but when an element in the form of a gas is suitably excited it emits a discontinuous spectrum which consists of lines or bands. Line spectra are produced by atoms whereas band spectra, which can often be resolved into closely spaced lines, are produced by molecules. Line spectra are much simpler than band spectra, which will not be considered here.

EXCITATION OF SPECTRA

The spectrum of an element can be excited in various ways. If the element or a volatile compound such as the chloride is heated in a bunsen flame it will produce a characteristic colour, e.g. yellow for sodium, lilac for potassium, and this is a useful method of identification. When the yellow light emitted by sodium chloride is examined with a low resolution spectroscope it is found to consist of a single yellow line. Spectra can also be excited by means of an arc. Flame and arc spectra are easily excited and the lines produced are mainly due to normal atoms. By passage of an electrical discharge through a gas at low pressure or by means of a spark discharge, additional spectral lines can be produced. In this case the potentials used are frequently high and the spectra are those of atoms in an excited state which have lost one or more electrons. The wavelengths of the new lines are shorter, i.e. the spectrum is extended towards or into the ultraviolet. The visible portion is only one section of the spectrum and the use of photographic plates and quartz spectrometers enable a spectrum to be mapped far into the ultraviolet. Lenses and prisms made from rock salt can be used for mapping the infrared. Thus the whole range of the optical spectrum can be covered.

When the flame or arc spectrum of a given element is compared with the spark spectrum of the adjacent element one place higher in the periodic table, a remarkable resemblance is observed. This is because the spark spectrum is produced by a singly ionised atom which has the same number of electrons as an uncharged atom of the element one place lower in the periodic table. By producing sparks at higher voltages a second or even a third spark spectrum can be observed and the resemblance can be extended successively to adjacent elements of lower atomic number. The additional spectra produced are those of atoms which have lost two and three electrons respectively.

EMISSION AND ABSORPTION SPECTRA

When the flame spectrum of an element such as sodium is observed against a bright light source emitting a continuous spectrum the yellow line appears as a dark line. This is known as an absorption spectrum. A well-known example of this is to be found in the spectrum of the sun. A series of fine dark lines can be seen called the Fraunhofer lines. These dark lines are the absorption spectra produced by elements present in the solar atmosphere, which is much cooler than the central mass of the sun. By comparing these lines with the emission spectra of known elements it is possible to identify elements present in the sun.

THE SPECTRUM OF HYDROGEN

As might be expected, the spectrum of the lightest element is the simplest of all atomic spectra. In 1885 Balmer first observed that the wavelengths of the lines in the visible spectrum of hydrogen could all be expressed in terms of a common formula:

$$\frac{1}{\lambda} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \tag{4.2}$$

where λ is the wavelength in centimetres, $m = 2$ and n can have any integral value greater than 2. The value of $R = 109677{\cdot}76\ \text{cm}^{-1}$. This is known as the Rydberg constant. $1/\lambda$ is often called the "wave number". The unit is cm^{-1}. Following the work of Balmer, Lyman found a similar series in the ultraviolet in which the $m = 1$ and n has integral values greater than 1. Three more series have been found in the infrared, named after their discoverers, Paschen, Brackett and Pfund in which m has the values 3, 4 and 5 and n integral values greater than 3, 4 and 5 respectively. These results may be summarised as shown in Table 4.1.

TABLE 4.1

	Hydrogen series of spectral lines	
	m	*n*
Lyman	1	2, 3, 4, etc.
Balmer	2	3, 4, 5, etc.
Paschen	3	4, 5, 6, etc.
Brackett	4	5, 6, 7, etc.
Pfund	5	6, 7, 8, etc.

It should be clear from the foregoing that the lines in any one series become closer and closer together as the value of n increases and finally reach a convergence limit when $n = \infty$.

The remarkable discovery of Balmer and others that the apparently complex system of lines in the hydrogen spectrum could be reduced to an ordered arrangement in this simple way showed that there must be some underlying principle responsible for the production of spectra. This principle is concerned with the structure of the atom.

SPECTRAL SERIES OF OTHER ELEMENTS

The spectra of elements other than hydrogen are naturally more complex, but it is generally possible to sort them out and to arrange them in series expressed by a similar formula to hydrogen, though the values of m and n are not necessarily integral. In general there are four distinct series which are named Sharp, Principal, Diffuse and Fundamental, respectively. The Principal series consists of the brightest lines. The lines of the Sharp and Diffuse series differ somewhat in appearance though these differences are marginal. The Fundamental series was so called because, at the time of its discovery, it was thought to have particular significance as its terms differ but little from those of the hydrogen series. The series is not really fundamental and might perhaps be better known as the " Bergmann " series, after its discoverer. However, the original name needs to be retained as the four series are designated by the letters S, P, D, F.

FINE STRUCTURE

When spectral lines are examined with a high resolution spectrometer they are found to show multiplicity, i.e. to have a fine structure. The familiar yellow line of sodium, which is the first in the Principal series of that element is found to consist of two very fine lines. All the spectral lines of the alkali metals consist of doublets. The spectral lines of the alkaline earth or group II elements show singlet or triplet structure. Group IIIa elements show doublets and quartets and higher groups show even greater multiplicity.

The quantum theory

BLACK BODY RADIATION

A black body is defined as a perfect absorber of radiation. The spectral distribution of the energy radiated is a function of the absolute temperature. Such a spectrum is called " black body radiation ". The nearest approach to a perfect absorber is a surface coated with lamp black. The colour of the light emitted by this surface changes from red at 700°K to white at 1650°K.

The laws which govern the emission and the distribution of the energy in the spectrum of a black body have been measured very

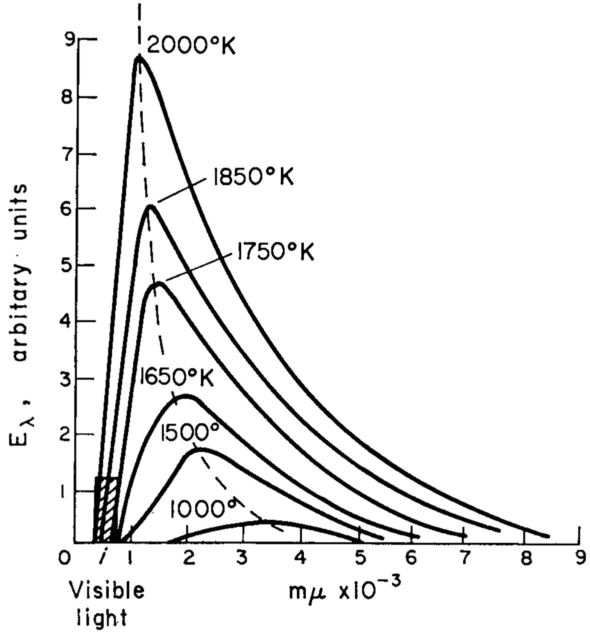

FIG. 4.5. The distribution of energy in the spectrum of a black body at different temperatures.

precisely. It has been shown that the total energy emitted increases rapidly with temperature and follows a fourth power law. Expressed mathematically:

$$E_{(\text{total})} = kT^4 \tag{4.3}$$

where T is the absolute temperature and k is a constant. The distribution of the energy, on the other hand, has a maximum value for a particular wavelength, which wavelength is inversely proportional to the absolute temperature (Fig. 4.5). Numerous attempts have been made to reconcile these observations with the classical wave theory. These attempts were based on the assumption that energy was emitted continuously by small vibrating molecules to which the law of equipartition of energy was applicable. This law states that the total energy of a system must be equally divided between the various degrees of freedom.

Rayleigh applied this principle to a system of vibrating molecules and showed that if there are n vibrations per second the rate of radiation of energy by such a system would be proportional to n^2. It follows that as the frequency increases so the total number of vibrations per second will increase. This would cause the rate of radiation of energy to increase and tend to infinity as the wavelength approached zero. This is not in accordance with the observations shown in Fig. 4.5.

THE QUANTUM THEORY

In 1901 Max Planck put forward a revolutionary theory that the energy was not emitted continuously but in a series of small packets which he called *quanta* (singular *quantum*). The value of the quantum was directly proportional to the frequency of the radiation, the proportionality constant being a universal constant of nature to which he gave the symbol h. Expressed mathematically,

$$E = h\nu \tag{4.4}$$

where ν is the frequency. The essential difference between the classical and quantum theories is that the classical theory assumes that each vibrating molecule radiates continuously, whereas Planck's quantum postulate assumes that the energy is emitted in a short pulse. On the basis of this theory, taking

$$h = 6{\cdot}55 \times 10^{-27} \text{ erg sec},$$

Planck was able to account for the shape of the curve (Fig. 4.5). Note that the constant h has the dimensions of action, i.e. energy × time.

THE PHOTO-ELECTRIC EFFECT

In 1902 Lenard made the important observation that electrons could be released from a metal surface by the action of light, and further, that the energy of the electrons was directly proportional to the frequency of the light. Below a certain frequency which was a characteristic of the metal, no electrons were released. Increasing the intensity of the light increased the number of electrons emitted per second but did not alter their energy. This again was contrary to the classical theory.

In order to measure the energy of the liberated electrons a grid was placed in front of the metal and a negative voltage applied to the grid until the flow of electrons stopped (Fig. 4.6). If V is the applied voltage and ν the frequency of the light, then

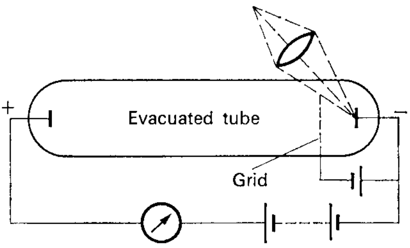

FIG. 4.6. The photoelectric effect.

$$V = k\nu - V_1 \tag{4.5}$$

where k is a constant independent of the metal employed and V_1 depends on the metal. Multiplying the equation by e, the electronic charge, and rearranging gives

$$eV + eV_1 = ke\nu, \tag{4.6}$$

where eV is equal to the kinetic energy of the electrons, hence $ke\nu$ must also have the dimensions of energy. Since the dimensions of ν are $\sec^{-1}$ it follows that ke has the dimensions of action, i.e. energy × time. If a graph is plotted of eV against ν, the slope of the graph gives the value of ke. This value is found to be equal to $6{\cdot}55 \times 10^{-27}$ erg sec, i.e. the same value as Planck's constant h. This is a very important method of measuring h.

THE PHOTON

In 1905 Einstein proposed an important extension of Planck's theory to explain Lenard's work. He suggested that light be regarded as particulate, i.e. that the light energy travelled in packets which he called photons. The energy of the photon was equal to $h\nu$. In the photoelectric effect one photon liberated one electron, the energy of the electron being equal to the energy of the photon, less the work required to detach the electron from the metal surface (eV_1 in eqn. (4.6)). eV_1 is called the "work function" of the metal. This immediately explained why the intensity of the incident light determined the number of electrons emitted per second. Since $h\nu = eV -$ the constant eV_1, $h\nu$ can be expressed in the same units, i.e. electron volts.

Einstein's theory revived the original corpuscular theory of Newton, but in order to explain interference and diffraction, light must also have a wave property. It will be seen in the next chapter (p. 90) how the dual property of wave and particle can be extended to include matter.

The Rutherford–Böhr theory of the atom

In Rutherford's theory the nucleus was supposed to contain A protons equal in number to the mass number (see p. 117) and A–Z electrons, where Z is the atomic number. The idea of electrons being contained in the nucleus was supported by the emission of β-particles by certain radioactive elements (β-particles are high energy electrons). It was, however, very difficult to reconcile the stability of nuclei which contained both positive and negative charges closely packed together. As early as 1920 Rutherford had predicted the existence of a neutral particle and he was proved correct in 1932 when Chadwick obtained neutrons by bombarding beryllium atoms with α-particles. (For further details see *Nuclear* *and Radiochemistry* in this series.) The nucleus is now considered to consist of Z protons and $A-Z$ neutrons.

The electrons surrounding the nucleus were supposed to move in orbits like a miniature solar system, the attractive force of the nucleus being counterbalanced by the centrifugal force of the rotating electron. Böhr of Copenhagen, however, showed that this structure was fundamentally unstable since a charged particle, such as an electron, rotating in an electric field must radiate energy continuously; in consequence the electron would slow down and spiral into the nucleus. Moreover, there is the further difficulty of explaining spectral lines which according to the quantum theory of radiation should correspond to the emission or absorption of definite amounts of energy. An electron which was gradually slowing down would produce a continuous spectrum, not a line spectrum.

In order to overcome these difficulties Böhr produced a hypothesis involving two postulates. The first was that an electron behaved differently from a normal charged particle and did not obey the classical laws of electro-dynamics, i.e. it could rotate in a closed orbit in an electric field without losing energy. The second postulate assumed that an electron could jump from one orbit to another, but in so doing it emitted or absorbed a quantum of energy in the form of radiation. Each orbit in which an electron could rotate was termed a *stationary state*, now known as an *energy level.* Expressed mathematically the permitted orbits were determined by the condition that the angular momentum of the electron must be an integral multiple of $h/2\pi$ units.

Böhr applied these ideas to the hydrogen atom. For simplicity he regarded the electron as moving in circular orbits. Let r be the radius of any given orbit, m the mass of the electron and v the velocity. Then the momentum of the electron is mv and its angular momentum is mvr. The product of angular momentum and angle has the dimensions of action (ml^2t^{-1}), so that Böhr* assumed that the " action " of the electron would be an integral multiple of

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* Strictly this explanation is due to Sommerfeld.

Planck's constant, the atom of action, i.e.

$$mvr \times 2\pi = nh$$

or

$$mvr = \frac{nh}{2\pi} \tag{4.7}$$

and

$$r = \frac{nh}{2\pi mv} \tag{4.8}$$

This is the mathematical formulation of Böhr's first postulate, where n stands for a series of integral numbers, these numbers being known as quantum numbers. The value of the quantum number determines the order of the orbit, i.e. when n is 1, r has the lowest possible value.

The value of r cannot be determined from eqn. (4.8) since v is unknown, but it is possible to eliminate v in the following way.

Let e be the charge on the electron. Then according to Coulomb's law the force of attraction between the hydrogen nucleus and the electron would be e^2/r^2. This force of attraction must be balanced by the centrifugal force mv^2/r, due to the rotation of the electron in the orbit.

Hence

$$\frac{e^2}{r^2} = \frac{mv^2}{r} \tag{4.9}$$

or

$$v^2 = \frac{e^2}{mr} \tag{4.10}$$

Squaring eqn. (4.8) and substituting for v^2 from eqn. (4.10) gives

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

or

$$r = \frac{n^2h^2}{4\pi^2me^2} \tag{4.11}$$

If the known values of h, m and e are substituted in the equation, the value obtained for r when $n = 1$ is of the correct order of magnitude ($0{\cdot}5 \times 10^{-8}$ cm), as determined by independent methods.

The total energy E of the electron is the sum of its kinetic energy ($\frac{1}{2}mv^2$) and its potential energy ($-e^2/r$). (This expression for the potential energy can be obtained by evaluating the work which must be done on the electron to remove it from a given orbit to infinity; see Appendix 1.) Hence

$$E = \tfrac{1}{2}mv^2 - \frac{e^2}{r}$$

but from eqn. (4.9)

$$\tfrac{1}{2}mv^2 = \frac{e^2}{2r}$$

Hence
$$E = \frac{e^2}{2r} - \frac{e^2}{r}$$

$$= -\frac{e^2}{2r} \qquad (4.12)$$

The negative sign indicates that energy must be supplied to the electron to remove it from the nucleus.

Substituting for r in eqn. (4.11) from eqn. (4.12) gives

$$-\frac{e^2}{2E} = \frac{n^2h^2}{4\pi^2me^2}$$

or
$$E = -\frac{2\pi^2me^4}{h^2} \cdot \frac{1}{n^2} \qquad (4.13)$$

where E is the energy of the electron in the orbit corresponding to a particular value of n. Since from eqn. (4.11) the value of r is directly proportional to n^2, the smaller the radius of the orbit the greater will be the liberated energy when the electron enters that orbit from outside, and conversely.

Böhr's second postulate can also be expressed in terms of action. Let ν be the frequency of the emitted radiation. Then

$$E_2 - E_1 = h\nu \qquad (4.14)$$

where E_1 and E_2 are the energies of the electron in the two different orbits concerned.

Applying this postulate to the energy liberated when an electron jumps from an outer to an inner orbit gives

$$E_{n2}-E_{n1} = h\nu = \frac{hc}{\lambda} = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

where c is the velocity of light, λ the wavelength and n_1 and n_2 the quantum numbers corresponding to the energy levels E_1 and E_2.

or

$$\frac{1}{\lambda} = \frac{2\pi^2 me^4}{h^3 c}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \tag{4.15}$$

This equation is similar to (4.2), i.e.

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

If the known values of m, e, h and c are substituted in the expression, the value of R' is found to be equal to 109,600 which is in remarkable agreement with the value of the Rydberg constant as determined experimentally.

At this stage it should be made clear that there was at that time no theoretical reasoning behind either of Böhr's postulates. They agreed with Planck's quantum theory and Einstein's equation for the photoelectric effect, $h\nu = E$, but the main justification for their use was that they worked. By application of this theory Böhr was able to calculate the wavelength of the main lines of the spectrum of hydrogen and hydrogen-like atoms or ions such as He^+ and Li^{2+}, etc., with remarkable accuracy, and also the radius of the hydrogen atom.

QUESTIONS

4.1. The values of $1/\lambda$, i.e. the wave numbers for the first five terms in the Lyman series for hydrogen are:

n	$1/\lambda$
2	82259·1
3	97492·3
4	102823·9
5	105291·6
6	106632·1

Plot these wave numbers against the corresponding values of $1/n^2$ and determine the value of $1/\lambda$ for $n = \infty$ eq. (4.2). From this calculate the convergence frequency and hence the ionisation energy in electron volts (see Chapter 5, p. 85).

4.2. Discuss the significance of Moseley's work in the advancement of chemical theory.

4.3. Sodium was exposed *in vacuo* to monochromatic radiation of various wavelengths. A grid was arranged in front of the metal and a negative voltage applied to the grid, as in Fig. 4.6. An electrometer was connected to the grid and the deflection recorded for various applied voltages over a fixed time. Table 4.2. shows the electrometer deflections observed for different applied voltages at three wavelengths.

TABLE 4.2

Wavelength 5461 Å		3650 Å		3126 Å	
Applied voltage	Electro-meter deflection	Applied voltage	Electro-meter deflection	Applied voltage	Electro-meter deflection
−2·257	28	−1·157	67·5	−0·5812	52
−2·205	14	−1·105	36	−0·5288	29
−2·152	7	−1·0525	19	−0·4765	12
−2·100	3	−1·0002	11	−0·4242	5
—	—	−0·9478	4	−0·3718	2·5

(*a*) Plot the deflection observed against the voltage for each wavelength and determine the minimum voltage required to prevent electrons from reaching the grid (see eqn. 4.5)).

(*b*) Convert the wavelength to frequencies (footnote, p. 65) and plot the minimum voltages as determined in (*a*) against the frequencies. Measure the slope of the graph (k in eqn. (4.5)) and from the known value of the electronic charge, $4{\cdot}81 \times 10^{-10}$ e.s.u. determine the value of Planck's constant h (eqn. (4.6)).

Note: To convert volts to e.s.u. divide by 300. (For further details of this experiment see Millikan, *Phys. Rev.* **7**, 355, 1916.)

4.4. The first ionisation energy for mercury is 10·4 eV. The frequency of the spectral line corresponding to this energy term is $2{\cdot}526 \times 10^{15}$ sec^{-1}. From these figures calculate the value of Planck's constant. (See Laurence, *Phys. Rev.* **28**, 947, 1926.)

4.5. When light falls on a metal surface in a vacuum, electrons may be emitted from the surface. What condition has to be satisfied if this phenomenon (the photoelectric effect) is to occur?

How does (*a*) the energy, and (*b*) the rate of emission of the photoelectrons depend upon the intensity and the wavelength of the incident light?

EITHER explain the relations you quote as fully as possible, OR describe how they may be demonstrated experimentally. (O. & C. G.C.E.)

4.6. When gold foil is bombarded with α-particles a few of them suffer deflections approaching 180°. It may be assumed that the α-particle begins to reverse its direction when its kinetic energy is equal to the potential energy of repulsion. The repulsive force between two charges is equal to $(e_1 \times e_2)/r^2$, where r is the distance apart; the corresponding potential energy is $(e_1 \times e_2)/r$. Calculate the effective radius of the nucleus of a gold atom from the following data: mass of the hydrogen atom $= 1{\cdot}65 \times 10^{-24}$ g, velocity of the α-particle $= 2 \times 10^9$ cm sec^{-1}, electronic charge $= 4{\cdot}8 \times 10^{-10}$ e.s.u. Assume that the radius of the gold nucleus is equal to the distance apart of the centres of the two nuclei when the α-particle reverses its direction.

CHAPTER 5

THE DEVELOPMENT OF THE WAVE MECHANICAL MODEL OF THE ATOM

Introduction

THE Rutherford–Böhr atom, as discussed in the last chapter, gave a rational explanation of the scattering of α-particles by metal foils and also agreed with Planck's quantum theory as applied to the spectre of hydrogen-like atoms. In its simple form, however, it proved to be inadequate to account, even in a qualitative way, for the spectra of other elements and modifications became necessary.

Extension of the Böhr theory

To explain the fine structure of the spectral lines (p. 69), Sommerfeld proposed that the electron could rotate in elliptical as well as circular orbits and introduced an azimuthal or subsidiary quantum number determining the ratio of the major to the minor axis of the ellipse. Two further quantum numbers had to be added called the *magnetic* quantum number and the *spin* quantum number. The magnetic quantum number was to account for the Zeeman effect — the splitting of the spectral lines in a magnetic field. The spin quantum number referred to the spin of the electron which was supposed to rotate like a top one way or the other, and so to cause the multiplicity of the spectral lines.

Detailed electronic structure of the Rutherford–Böhr–Sommerfeld atom

This theory supposes the nucleus to be surrounded by electrons, particles spinning on their axes and moving in orbits arranged in energy levels at varying distances from the nucleus. Reckoned outwards the levels are given principal quantum numbers of 1, 2, 3, 4, etc., and each level can accommodate a maximum of two, eight, eighteen, and thirty-two electrons respectively. The outermost level in a free atom never contains more than eight electrons and the next level never more than eighteen. The electrons in each main level are divided into sub-levels called *s*, *p*, *d* and *f*; the energy of each sub-level is determined by the value of the subsidiary or azimuthal quantum number. The *s* sub-level contains a maximum of two electrons, the *p*-sub-level six, the *d* sub-level ten and the *f* sub-level fourteen. The first quantum level can only contain *s* electrons, the second *s* and *p*, the third *s*, *p* and *d*, and the fourth *s*, *p*, *d* and *f*.

The shape of the electronic orbits is determined by the value of the azimuthal quantum number. The orbit of the *s* electrons is circular while the orbits of the *p*, *d* and *f* electrons are elliptical, the ratio of the major to the minor axis being 1 for the *s* orbit, 2 for the *p*, 3 for the *d* and 4 for the *f* orbit. Only two electrons can be accommodated in any given orbit and their spins must be opposed. Each electron has its own particular set of quantum numbers, the principal quantum number (n), the azimuthal quantum number (l)* determining the ratio of the major to the minor axis of the ellipse, the magnetic quantum number (m) determining the orientation of the orbit in space, and the spin quantum number (s) determining the direction of spin. *In any one atom there is never more than one electron with the same set of quantum numbers. This is known as Pauli's exclusion principle.*

The values of the quantum numbers are related as follows: the principal quantum number (n) has integral values of 1, 2, 3 and 4, etc. The azimuthal or subsidiary quantum number (l) can have values $0 \rightarrow (n-1)$. The magnetic quantum number (m) can have values of $-l$ through 0 to $+l$ and the spin quantum number (s)

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* Sommerfeld's original symbol for the azimuthal quantum number was k and its minimum value was 1. This was soon shown to be incorrect; the azimuthal quantum number can have a value of 0. This clearly has no meaning when related to an orbit. In the modern theory the symbol l is used to replace k.

values of either $+\frac{1}{2}$ or $-\frac{1}{2}$. Thus when $n = 1$, l and m must be 0 and s can be $\pm\frac{1}{2}$. This allows two electrons only in the first level. When $n = 2$, l can be 0 or 1, $m - 1$, 0 or $+1$ and $s \pm\frac{1}{2}$. This allows a maximum of eight electrons in the second level, two s electrons travelling in a circular orbit with $l = 0$ and $m = 0$ and six p electrons in three different orbits with $l = 1$ and $m = -1$, 0 or $+1$. Each electron can have two possible values of s, $\pm\frac{1}{2}$. This gives a different set of quantum numbers to each electron in the second quantum level. Similar reasoning shows that eighteen electrons can be permitted in the third level, two s, six p, and ten d electrons, and that the fourth level can contain two s, six p, ten d and fourteen f electrons.

EXAMPLE. Oxygen with a total of eight electrons has two electrons in the first quantum level or K shell (p. 84) which is completely filled since l and m must both be 0. The remaining six electrons are in the second quantum level or L shell, two with $l = 0$, $m = 0$, two with $l = 1$, $m = 0$, one with $l = 1$, $m = 1$ and one with $l = 1$, $m = -1$. It will be noticed that four of these six electrons are paired, that is to say they have the same values of n, l and m and only differ in their value of s. The remaining two electrons are unpaired because they have the same values for n and l but different values for m. Böhr's picture of the electrons of oxygen in the second quantum level would be two electrons travelling in a circular orbit with opposed spins, two electrons in an elliptical orbit with opposed spins and the remaining two electrons in two separate elliptical orbits. All three elliptical orbits are inclined to one another, i.e. have different orientations in space. The two unpaired electrons give oxygen a covalency of 2 because two further electrons can be accommodated in the last two orbits provided their spins are opposed. Covalency bonds are formed by the pairing of electrons with opposed spins in the same orbit. The subject of valency is discussed in detail in the volume *Chemical Binding and Structure* of this series.

The Rutherford–Böhr theory was also able to explain the spectral series in the spectrum of atomic hydrogen. The Lyman series is produced by an electronic transition from a series of outer energy levels, or orbits in this model of the atom, to the energy level nearest to the nucleus. The other series are similarly produced by transitions from outer levels to the second, third, etc., level. With the modifications introduced by Sommerfeld, it is also possible to explain in a qualitative way the spectral series of other elements, but in particular the theory explains the origin of X-ray spectra.

TABLE 5.1. ELECTRONIC STRUCTURES FOR SOME OF THE LIGHTER ELEMENTS SHOWING THE VALUES OF THE AZIMUTHAL AND MAGNETIC QUANTUM NUMBERS

Main levels			*K* $n = 1$	*L* $n = 2$		*M* $n = 3$		
Sub-levels			*s*	*s*	*p*	*s*	*p*	*d*
Element	Number of electrons = atomic number	Values of l	0	0	1	0	1	2
		Values of m	0	0	0−1+1	0	0−1+1	0−2−1+1+2
Li	3		2	1				
N	7		2	2	1 1 1			
O	8		2	2	2 1 1			
Cl	17		2	2	2 2 2	2	2 2 1	
A	18		2	2	2 2 2	2	2 2 2	

It will be recalled that X-rays are a form of electro-magnetic radiation of high frequency, i.e. the quantum of energy $h\nu$ associated with them is considerably larger than for visible light. X-rays are produced by bombarding an element with high energy electrons. The energy associated with these electrons is large enough to dislodge electrons from the inner levels of the atom. X-rays are emitted when an electron from an outer level moves in to fill the vacancy. The innermost level is referred to as the *K* shell, the second as the *L* shell, the third as the *M* shell, etc. The most penetrating X-rays, i.e. the *K* series, are produced by transitions from outer levels to the *K* shell and the K_α lines are caused by the transitions from the *L* shell to the *K* shell; similarly, the *L* series is produced by transitions to the *L* shell. The values of the quantum numbers for the shells are 1 for *K*, 2 for *L*, etc.

If the *K* series of X-rays is excited it is found that the other series are simultaneously produced. On Böhr's theory this clearly must be so since a transition from an *L* level to a *K* level producing the K_α line must leave a vacancy in an *L* level and so on for other levels.

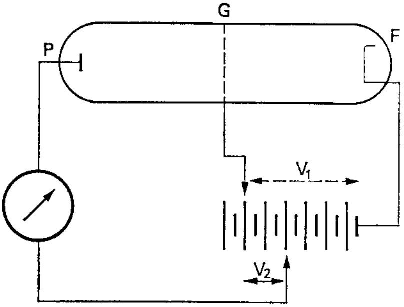


FIG. 5.1. The measurement of ionisation potential.

Ionisation potentials

Convincing evidence for this theory of atomic structure comes from a study of ionisation potentials. Ionisation potential is defined as the potential required to accelerate electrons to a sufficient energy to ionise an atom by an inelastic collision. The energy is conveniently measured in electron volts (eV). An electron volt is defined as the energy acquired by an electron moving through a fall of potential of 1 V. The charge on the electron is $4{\cdot}802 \times 10^{-10}$ e.s.u. Converting this figure to e.m.u. by dividing by the velocity of light gives $1{\cdot}601 \times 10^{-20}$ e.m.u. or

$1{\cdot}601 \times 10^{-19}$ C. An electron volt is therefore equivalent to $1{\cdot}601 \times 10^{-19}$ V coulomb or joule, or $1{\cdot}601 \times 10^{-12}$ erg.

The measurement of ionisation energies has given proof of the number of electrons which exist both in the main and the subsidiary quantum levels around the nucleus. Several methods have been devised. The principle is shown in Fig. 5.1. An electrically heated filament *F* contained in a partially evacuated tube emits electrons which are accelerated towards a grid *G* by application of a positive potential V_1. The plate *P* is also maintained positive to *F* but slightly negative with respect to *G*. Electrons in the course of their passage from *F* to *G* undergo numerous elastic collisions

TABLE 5.2. THE FIRST AND SECOND IONISATION ENERGIES FOR ELEMENTS 1–20

Element	First ionisation energy (eV)	Second ionisation energy (eV)
H	13·0	—
He	24·6	54·4
Li	5·4	75·6
Be	9·3	18·2
B	8·3	25·1
C	11·3	24·4
N	14·6	29·6
O	13·6	35·1
F	17·4	35·0
Ne	21·6	41·0
Na	5·1	47·3
Mg	7·7	15·0
Al	6·0	18·8
Si	8·2	16·3
P	11·0	19·7
S	10·4	23·4
Cl	13·0	23·8
A	15·8	27·6
K	4·3	31·8
Ca	6·1	11·9

with the atoms or molecules of the gas in the tube. When the accelerating potential V_1 exceeds V_2, electrons pass through the grid and a current is indicated on the galvanometer. This current at first increases with increase of V_1 but at a certain critical potential current ceases to flow. This is because the electrons have lost their energy by undergoing an inelastic collision with gas molecules in the tube and so are unable to

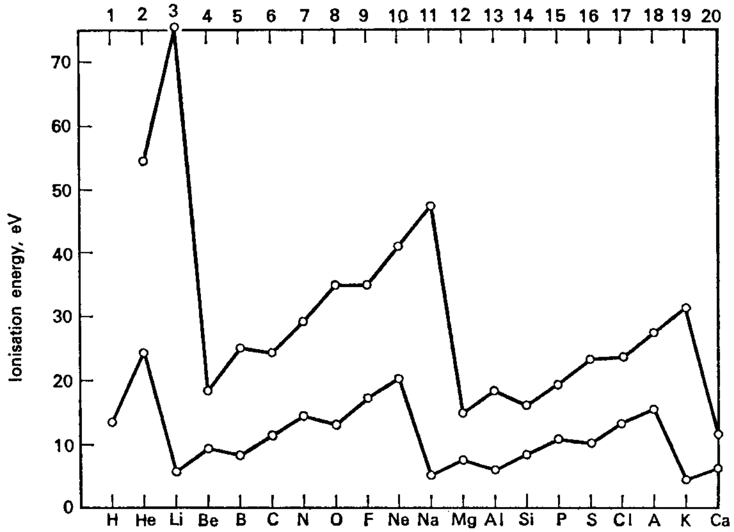


FIG. 5.2. First and second ionisation energies for the first twenty elements.

overcome the opposing potential V_2. Measurements of ionisation energy can also be carried out by using a thyratron or gas-filled triode containing the element in the form of a gas (expt. 5.1).

The results of these measurements for the first twenty elements can be seen in Table 5.2 and Fig. 5.2. The lower curve shows the first ionisation energy which corresponds to the energy required to remove one electron from the atom. The upper curve shows the second ionisation energy, i.e. the energy required to remove a second electron from the atom. It will be noticed that the peaks in the first curve all coincide with a noble gas and each noble gas is separated from the next by seven elements. It will also be noticed that the peaks in the upper curve are displaced exactly one element to the right. This shows that the ion produced by the loss of one electron has the electronic structure of the preceding element in the periodic table. Thus ionised lithium has the helium structure and to remove the second electron from lithium requires far more energy than that required to remove the first electron since the inner electron pair must be broken.

In particular the curve indicates:

1. The number of electrons occupying the various energy levels in the ground state of each element.
2. The division of the first three main levels into *s* and *p* sub-levels.
3. The number of electrons in each sub-level.
4. The completion of the *s* sub-level before the *p* sub-level can start to fill.

The break in the electron energy curve after three *p* electrons have been added shows that there are three distinct positions within the *p* subgroup and each position can accommodate two electrons. These " positions " were pictured by Böhr as orbits in which two electrons could rotate with opposed spins. They are now called orbitals (see p. 95). The *p* sub-level therefore contains three orbitals. As the atomic number increases the electrons first occupy vacant orbitals within any given sub-level and then pair up. This is called the principle of " maximum multiplicity ". The break in the curve corresponding to the filling of the *p* subgroup is thus explained.

The extended ionisation energy curve (Fig. 5.3) gives further striking evidence. The small change in the ionisation energies of the transitional elements is due to the expansion of the third and fourth energy level respectively from eight to eighteen electrons. It is clear that the third level can contain a maximum of eighteen electrons, the additional ten electrons filling the vacant *d* orbitals.

There are five *d* orbitals which can each accommodate two electrons with opposed spins. The expansion of the penultimate energy level accounts for the remarkable lateral resemblances of these elements. The sharp stepwise rise at the end of the transition series follows the same pattern as is seen in periods two and three and is caused by the filling of the 4*p* and 5*p* orbitals respectively. In the sixth period there is an almost horizontal section corresponding to the rare earth or lanthanide group of fourteen elements. This is due to the expansion of the fourth energy level from eighteen to thirty-two electrons. The fourteen electrons added fill the vacant 4*f* orbitals deep inside the atom. Another transition series follows the lanthanides with the completion of the 5*d* orbitals and, finally, we see the filling of the 6*p* orbitals culminating in radon.

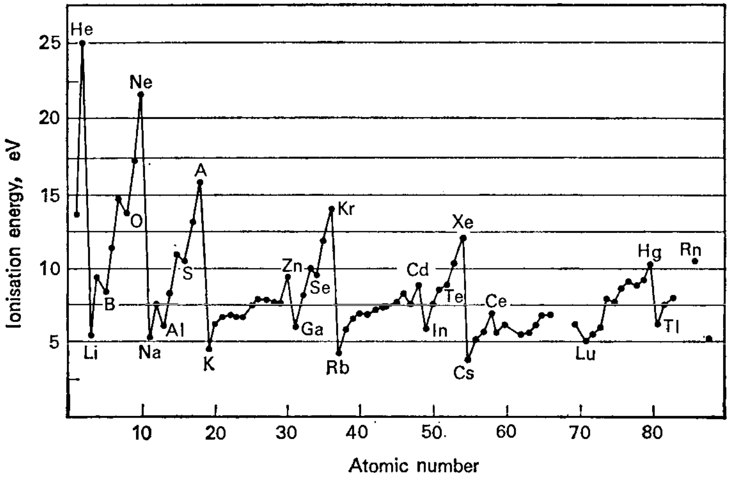


FIG. 5.3. Variations in first ionisation energy with atomic number.

The anomalous high peak of mercury should be noted. This is due to the remarkable stability of the 6*s* orbital. Mercury approaches the properties or absence of properties of a noble gas and its first ionisation energy lies very close to a curve drawn through the values for the noble gases. The big drop from mercury to thallium shows the stability of the thallous ion and the ease of removal of a 6*p* electron compared to a 6*s* electron. This effect is carried on through the remainder of the sixth period and is well shown by the stability of Pb^{2+} and Bi^{3+} ions.

Ionisation energies and chemical properties

It is instructive to compare some of the characteristic features of the periodic table as detailed on pages 21–22 with the ionisation energy curve (Fig. 5.3). For convenience of reference the paragraphs are numbered similarly.

1. The number of elements which can fit into each period is determined exactly by the principal breaks in the curve.
2. The arrangement of the elements in groups with recurring properties agrees with their position on the curve.
3. The resemblances of the typical elements to sub groups Ia, IIa, IIIb to VIIb is seen to be natural and follows the shape of the curve.
4. The strongly electro-positive elements on the left-hand side of the periodic table are at the points of low ionisation potential; the converse is also true.
5. Fluorine, the most electro-negative element has the highest ionisation potential apart from helium and neon, whereas caesium, the most electro-positive natural element has the lowest.
6. The lateral resemblances of the transitional elements are to be expected from the much less steeply inclined part of the curve compared to regions covering groups IIIb to VIIb.
7. The rare earths coincide with an almost horizontal section of the curve which accounts for their even more marked lateral resemblances.

Finally, if lines are drawn across the graph linking the elements in subgroups IIa and IIIb–VIIb it will be noticed that the line drops much more steeply between the first two elements in the group than between succeeding elements. This accounts for some of the " peculiar " properties shown by the first member of a group.

Weaknesses of the Böhr–Sommerfeld treatment

This theory gives a nice tidy picture, explains the spectrum of hydrogen and hydrogen-like atoms, e.g. He^+ and Li^{2+}, enables the atomic radius to be calculated and accounts in a most satisfactory manner for the curve of ionisation energies. It fails, however, to explain the spectrum of normal helium, nor does it explain the varying intensity of the spectral lines. It suffers from the drawback that it uses classical mechanics to determine the path of an electron, but introduces two arbitrary postulates: the system of stationary states and the quantization of action. Moreover it takes no account of the wave properties of the electron and Heisenberg's uncertainty principle, both of which are discussed in the next section. For these reasons the Böhr–Summerfeld theory has now been abandoned though it is still useful for elementary calculations. Its value in the advancement of our knowledge of atomic structure must not be underrated, and it is for this reason that it has been described in some detail.

The wave mechanical treatment

THE DUAL NATURE OF MATTER

In 1924 Prince Louis de Broglie, a student who was studying for his doctorate, developed a most daring theory in his thesis. He was warned by his tutor that he was most unwise and that the thesis would probably be rejected, but despite this warning de Broglie proceeded. He argued that Einstein's theory of the photoelectric effect implied a return to the corpuscular theory of Newton. Light photons being particulate must possess momentum and de Broglie showed that this momentum must be equal to h/λ, where h is Planck's constant. Since photons also had wave-like properties he suggested that electrons, and in fact, all matter, should similarly have wave-like properties, and proposed the equation

$$\lambda = \frac{h}{mv} \tag{5.1}$$

connecting the wavelength with the mass and velocity of the particle. For particles of macroscopic size the value of λ would be so small that wave-like properties could not be detected, but an electron with a mass of the order of 10^{-27} g moving with a velocity one-tenth of the velocity of light should have a wavelength similar to that of X-rays.

Equation (5.1) can also be written

$$\lambda = \frac{h}{\sqrt{(2m \cdot \frac{1}{2}mv^2)}} \tag{5.2}$$

showing that the wavelength should be inversely proportional to the square root of the kinetic energy.

De Broglie predicted that electrons would show interference and diffraction effects and his theory was conclusively proved 3 years later when Davisson and Germer showed that electrons could give diffraction patterns when reflected from the surface of a nickel crystal and they verified the equation $\lambda = h/mv$ within the limits of experimental error. The wave properties of electrons are used in the electron microscope, which perhaps gives the most striking experimental evidence for de Broglie's theory.

A more recent instrument, known as the field emission microscope, invented by E. W. Müller, gives still greater magnification. This uses electrons emitted by a very fine tungsten mono-crystal as cathode in a highly evacuated glass bulb. A voltage of about 10 kV is commonly employed. The electrons fall on a fluorescent screen fitted on the glass bulb and give a pattern which depends on the material on the tungsten crystal. If a barium anode is used, barium atoms are deposited on the crystal and can be seen as dots on the fluorescent screen. If the crystal is heated, the barium atoms are agitated and are torn away by impulses due to the lattice vibrations giving an image of vigorous swarm movement. The actual movements of the atoms can thus be seen. With the aid of this instrument, Müller was able to obtain a picture of the copper phthalocyanine molecule which showed its four-leaf clover shape, thus confirming the structure as deduced by theoretical organic chemistry. Field emission microscopes can now be obtained from suppliers and are relatively inexpensive.

If de Broglie's theory is applied to an electron moving in an orbit, it is immediately clear that only those orbits are permitted which could contain an integral number of wavelengths, i.e.

$$2\pi r = n\lambda \tag{5.3}$$

and since

$$\lambda = \frac{h}{mv} \text{ (eqn. (5.1))}$$

$$2\pi r = \frac{nh}{mv}$$

and

$$r = \frac{nh}{2\pi mv}$$

This is, in fact, Böhr's first postulate (p. 75). The argument only applies to a particle constrained to move in a circular orbit, whereas de Broglie's hypothesis applies to free particles also. Nevertheless, the deduction is of interest.

THE UNCERTAINTY PRINCIPLE

This principle, which is fundamental to all scientific measurement, was put forward by Heisenberg in 1927. He showed that it was impossible to measure exactly both the position and the momentum of a moving particle. His argument as applied to an electron may be summarised as follows: to determine the position of a moving electron it is necessary to observe it with some form of radiation. Since the maximum resolving power of a microscope is limited to half a wavelength, visible light would be of no use since the wavelength is about one million times the diameter of an electron. Suppose it were possible to construct a gamma-ray microscope using gamma rays of wavelength 10^{-11} cm, then from eqn. (5.1) the momentum of the gamma photons would be

$$\frac{6 \times 10^{-27}}{10^{-11}} = 6 \times 10^{-16} \text{ g cm sec}^{-1}$$

Suppose the electron were moving with a velocity one-tenth of the velocity of light. Then the momentum of the electron would be

$$10^{-27} \times 3 \times 10^{9} = 3 \times 10^{-18} \text{ g cm sec}^{-1}$$

The momentum of the photon would be 200 times the momentum of the electron and the velocity of the electron would be altered very considerably. Though it would be possible to observe the subsequent path of the photon and to determine the position of the electron by calculation of the displacement of the photon due to the impact, this could only be done at the expense of changing the momentum of the electron.

To avoid any appreciable change in the momentum of the electron it would be necessary to use much less energetic gamma rays which would have too long a wavelength to enable the position of the electron to be determined with sufficient accuracy. The fundamental difficulty pointed out by Heisenberg is the interaction of measurer and measured. Heisenberg showed mathematically that if $\Delta(x)$ is the uncertainty or experimental error in measuring the position of a particle and $\Delta(mv)$ is the uncertainty in measuring the momentum, then

$$\Delta(x) \times \Delta(mv) = h \tag{5.4}$$

In theory this equation applies to all bodies, but in practice it is only significant for sub-atomic particles.

Equation (5.4) can be applied to other pairs of related quantities with a product which has the dimensions of $h\,(ml^2t^{-1})$ such as energy and time, and angular momentum and angle.

Thus
$$\Delta(E) \times \Delta(t) = h \tag{5.5}$$

and
$$\Delta(I) \times \Delta\theta = h \tag{5.6}$$

Consideration of eqns. (5.5) and (5.6) will show that there is an entirely different interpretation of the Rutherford–Böhr theory.

If the energy of the electron in a particular level is specified precisely, then the uncertainty in the measurement of the time is infinite. This means that it is impossible to specify the position of the electron, for as it is supposed to be rotating in an orbit its position can only be measured in terms of time. This leads to the idea of a stationary state, i.e. one where the energy remains constant for all time. (The student who wishes to convince himself of this should work out example 5.4.)

Heisenberg's principle shows that it is pointless to consider an electron in an atom as a particle rotating in an orbit, for the position of the particle cannot be determined. All that can be said is that there is a certain probability of locating the electron within a certain volume.

THE WAVE MECHANICAL ATOM

A few years after de Broglie put forward his theory, Erwin Schrödinger published his wave equation connecting the energy of an electron in an atom with the amplitude of the associated wave. Schrödinger realised that any adequate theory of atomic structure must incorporate the principles of the quantum theory to account for line spectra and must also include the wave properties of the electron. Standing waves associated with vibrating objects can be expressed by equations in which a set of integers naturally and necessarily appear. Thus a stretched string can vibrate only in certain ways corresponding to the fundamental and harmonic notes. Its vibrations can be expressed mathematically

$$y = A \sin n\pi \left(\frac{x}{l}\right)$$

where y is the amplitude, x the lateral displacement, l the length of the stretched string, A a constant, and n an integer. For the fundamental $n = 1$ and for the harmonics $n = 2, 3$, etc.

Schrödinger applied these ideas to a vibrating body producing spherical waves. The derivation of his equation is beyond the scope of this book; suffice it to say that his equation has certain finite solutions which correspond exactly to the energy levels of the older Böhr treatment. The advantages of the Schrödinger approach are that it avoids the arbitrary assumptions of the Böhr theory and gives a better interpretation of atomic spectra. It gives energy levels for the hydrogen atom in agreement with experiment as did the Böhr treatment, but in addition it gives the correct values for the energy levels of the helium atom where the Böhr theory failed. In addition it does not conflict with the uncertainty principle.

Schrödinger pictured the electron as a wave stretching from the centre of the atom to infinity. Such a picture is unrealistic. Max Born proposed that the wave was not the electron at all, but that the position of the electron, which could still be regarded as a particle, could only be expressed in terms of probability. In Schrödinger's equation the symbol Ψ represents the amplitude of the spherical wave. The square of the amplitude, Ψ^2 is proportional to the density of the wave and $\Psi^2 dv$ is the probability of finding the electron in a small element of volume dv.

If Ψ^2 for the $1s$ level is plotted against r, the distance from the centre of the atom, the graph has the form shown in Fig. 5.4. The value of Ψ^2 dies away and becomes 0 at infinity. However, it becomes exceedingly small at a very small value of r.

The probability of locating the electron can also be expressed in terms of a *radial probability distribution.* This means the chance of finding the electron in a spherical shell of radius r and thickness dr. The volume of such a shell is $4\pi r^2 dr$ and the probability of finding the electron in such a shell is $4\pi r^2\Psi^2$. Figure 5.5 shows the result of plotting this probability against r. The value of r for which $4\pi r^2\Psi^2$ is a maximum happens to correspond exactly to the Böhr radius.

The value of $4\pi r^2\Psi^2$ falls off rapidly with distance, but it is possible to choose a value for r such that there is a 90% chance of finding the electron within a sphere of this radius. For the hydrogen atom in its ground state this value of r is 2·6 times the Böhr radius. The volume of a sphere with this particular value of r is called the $1s$ orbital. There is a 90% chance of locating the electron within this volume when the hydrogen atom is in its lowest energy state. When the electron is raised to higher energy levels, the solution of the wave equation gives sets of values of Ψ^2, which give different shapes to the space distribution of the electron.

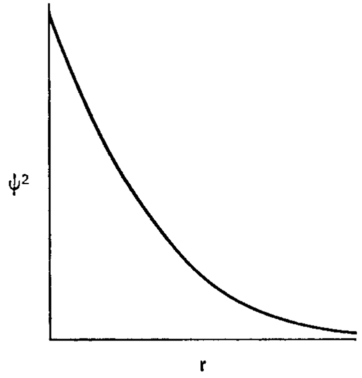


FIG. 5.4.

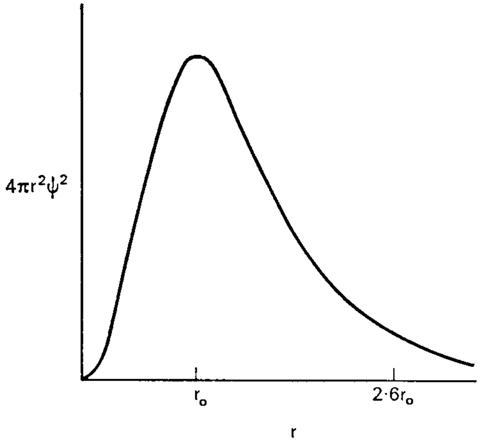
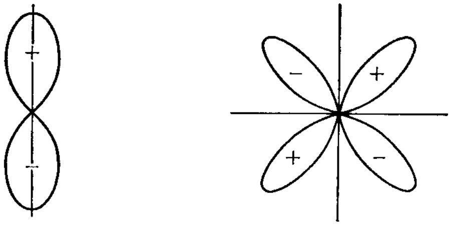


FIG. 5.5. r_0 represents the Böhr radius.

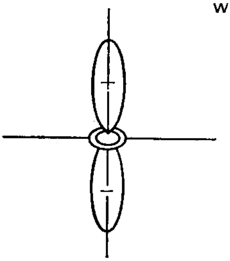
All the *s* levels are spherical while the three *p* levels are dumb-bell shaped. The five *d* levels give four-leaf clover patterns, with the exception of one *d* level, which is different. These shapes are represented in Fig. 5.6.

The wave mechanical model of the atom represents the positions of the electrons as clouds of varying charge density, the shapes of the clouds depending on the energy levels. The probability of locating the electron in any small element of volume depends on the charge density. Wave mechanics does not answer the question " What is the electron? " All that can be said is that it is neither wholly a particle nor wholly a wave though it has the properties of both. It can only be located in statistical terms.



p-orbital
three p-orbitals along the
x, y & z axes with m = 0, +1, -1

d-orbital
four d-orbitals of this shape,
three along the x, y & z axes
with m = +1, -1, -2 and one at 45°
with m = +2



d-orbital (m = 0)

FIG. 5.6. *p*-orbitals and *d*-orbitals.

EXPERIMENT

5.1. MEASUREMENT OF THE FIRST IONISATION POTENTIAL OF XENON

The following experiment due to Professor R. S. Nyholm is a modification of the Hertz method. The circuit is shown in Fig. 5.7. The 20 V supply can be obtained from a well-smoothed power pack, or batteries can be used. The 200 Ω variable potentiometer must be at least 2 W. The voltmeter must read to 15 V and the ammeter in the anode circuit 0–50 μA. The valve is a thyratron EN 91, which is easily obtainable from most radio shops.

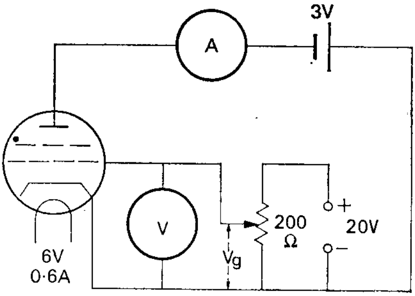


FIG. 5.7.

With the small negative potential applied to the anode, no current is observed in the anode circuit until V_g reads about 12 V. The electrons, accelerated towards the first grid, have now reached an energy corresponding to the first ionisation potential of xenon and the gas ionises. As the voltage applied to the grid is further increased the anode current increases but the reading of V_g now falls. This is due to a fall in the internal resistance of the valve with increasing ionisation. The student should plot a curve of anode current against grid potential. The curve should intersect the base line at 12·3 V.

The circuit can be easily adapted to make a striking demonstration. The microammeter is replaced by a 0·5 MΩ resister and the anode coupled through a 0·1 μF capacitor to a loud-speaker via a suitable amplifier. The other side of the amplifier is coupled to the cathode of the valve and is earthed. As V_g is increased steadily from 0 a rushing sound will be heard in the loud-speaker when the valve ionises.

QUESTIONS

5.1. Write a brief historical account of the development of our knowledge of the structure of the atom. [Oxford Schol.]

5.2. Why has the Böhr theory of atomic structure been replaced by the Schrödinger theory?

5.3. Write short notes on: Pauli's exclusion principle; the principle of maximum multiplicity; ionisation potential; uncertainty principle.

5.4. By application of Heisenberg's uncertainty principle, calculate the percentage error in measuring the time of revolution of an electron assumed to be rotating in the $2p$ orbit of a hydrogen atom (uncertainty in the energy of a $2p$ electron (ΔE) = 10^{-7} eV,* mass = $9{\cdot}11 \times 10^{-28}$ g, charge = $4{\cdot}81 \times 10^{-10}$ e.s.u., radius of the orbit = $0{\cdot}5 \times 10^{-8}$ cm, $h = 6{\cdot}55 \times 10^{-27}$ erg sec, 1 eV = $1{\cdot}60 \times 10^{-12}$ erg. *Note:* calculate the velocity of the electron and hence the time of revolution by use of eqn. (4.10)).

5.5. Calculate the ionisation energy in kilocalories per mole (g atom) from the observed first ionisation energies given in Table 5.2 for the elements hydrogen, lithium and fluorine.

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* This quantity can be measured from the width of the spectral line.

CHAPTER 6

THE DETERMINATION OF ATOMIC WEIGHTS

Introduction

THE DEFINITION of atomic weight has undergone a number of changes. The original definition suggested by Davy in 1812 was the weight of one atom of the element compared to the weight of one atom of hydrogen. This was logical in that gas densities were compared to hydrogen as the lightest gas and the comparison of the weights of equal volumes of gases was regarded as the comparison of the weights of the atoms. Berzelius was the first to introduce an oxygen standard 0 = 100 since his atomic weight determinations as explained on page 9 were based on combining weights the majority of which relied on combustion or reduction.

Ostwald introduced the scale 0 = 16 in 1885. This had the advantages of both scales. The atomic weights of most of the elements were approximately whole numbers as on the scale H = 1, but the values could be quoted with greater precision since the combining ratio element to oxygen was generally known more accurately than the ratio hydrogen to oxygen.

Within the last few years the oxygen standard has been abandoned and a carbon standard as one-twelfth of the carbon 12 isotope substituted. The reason for this change is two-fold. In the first place oxygen has been found to consist of a mixture of isotopes 16, 17 and 18. The physical standard had been based for a long time on the ^{16}O isotope but has recently been changed to ^{12}C, so that physical atomic weights were slightly different from chemical atomic weights. This difference was undesirable. Secondly, improvements in mass spectrometry have made it possible to measure chemical atomic weights with an accuracy equal to and in some cases better than the best analytical methods. Carbon is a much more suitable element than oxygen for use in a mass spectrometer, since it is possible to obtain carbon ions containing many carbon atoms (for example, benzene breaks down in a mass spectrometer to C_6^+). This means that exact multiples of the standard can be introduced at various points of the scale. In addition charged carbon hydrides can be used as reference lines. Most nuclear masses are related more closely to ^{12}C than to ^{16}O.

The constancy of atomic weights

At one time the atomic weight of an element was considered to be always constant and a fundamental property of the element. This is no longer accepted. The atomic weight will only be constant provided the proportion of the various isotopes does not vary. The classical case of the variation in the atomic weight of lead according as to whether it was obtained from a radioactive or non-radioactive mineral is well known and led to the discovery of isotopes. (This is dealt with more fully in *Nuclear and Radiochemistry* of this series.) Other elements such as boron and potassium show very slight variations according to their source and even oxygen obtained from the atmosphere is a few parts per million denser than oxygen obtained from natural waters due to a change in the proportion of ^{16}O to ^{18}O. Very slight differences exist in the chemical properties of isotopic compounds and these differences can be used to effect chemical separation of the isotopes of the lighter elements. The most striking case is that of hydrogen and deuterium, but chemical separations based on isotopic exchange reactions have been developed for carbon, nitrogen and sulphur. In atomic weight determinations based on chemical methods the possibility of some isotopic separation occurring as a result of the chemical operations has to be carefully considered.

Physical methods of determining atomic weights

These methods depend upon either the measurement of vapour density or the use of the mass spectrograph. Both are capable of high precision. The principles of vapour density determination will first be described together with a description of the use of the buoyancy and torsion balances. This will be followed by an account of the development of modern mass spectrographs and spectrometers beginning with the work of Sir J. J. Thomson on positive ray analysis.

THE VAPOUR DENSITY METHOD

This is suitable for gaseous elements or those which can be easily vaporised. It can also be used for measuring the atomic weights of solid elements by determining the vapour density of a gaseous compound of that element with an element of known atomic weight. An example is the measurement of the atomic weight of sulphur from the vapour density and hence molecular weight of sulphur dioxide; the atomic weight of sulphur is obtained by subtracting 2×16 from this molecular weight. The principle consists in comparing the density of the gas at a known temperature and pressure with the density of a standard gas such as oxygen, and multiplying the result by 16. The density has to be corrected to the *limiting density* which is the density at which Avogadro's law is strictly applicable.

LIMITING DENSITY

A normal gas shows deviations from the ideal gas laws due to the molecules occupying a definite fraction of the total volume and also exercising attractions on each other. For this reason the graph of PV against P at constant temperature is not parallel to the P axis but with the exception of hydrogen falls with increasing pressure at low pressures, passes through a minimum and then rises again (Fig. 6.1). The position of the minimum for a given gas depends on the temperature. For many gases the PV/P curve below about 1 atm is almost linear. The normal density in grams per litre per unit pressure is defined as W/PV. The limiting density is $W/(P_0 V_0)$. To determine this it is necessary to make several measurements of the density of the gas at different pressures below 1 atm and plot the value of W/PV against P, extrapolating the graph to zero pressure (Fig. 6.2). This gives the

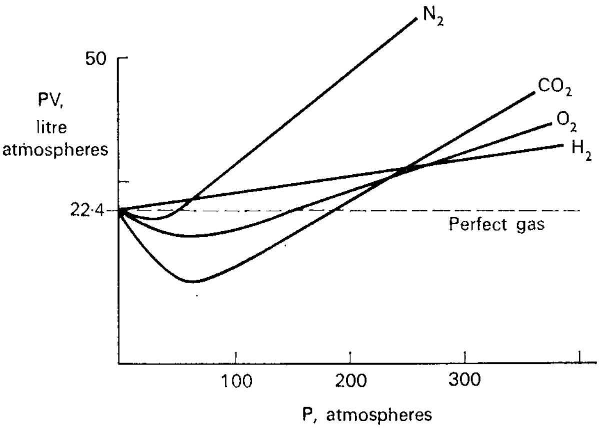

FIG. 6.1. PV/P curve for one mole of a gas at 0°C (50°C in the case of carbon dioxide). Note that hydrogen shows no minimum at this temperature.

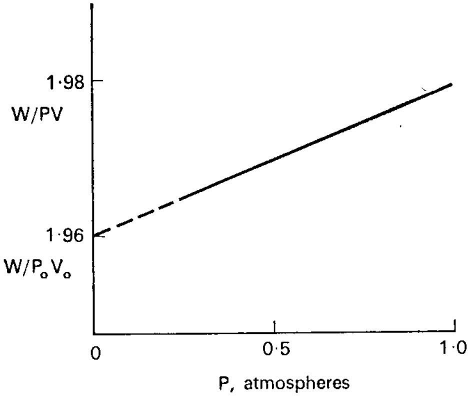

FIG. 6.2. Graph of W/PV against P for nitrous oxide.

value of the limiting density. From this the vapour density is determined by comparison with a standard gas and hence the molecular weight. Dividing the molecular weight of an elementary gas by the atomicity gives the atomic weight.

ATOMICITY

The atomicity can be deduced in some cases by chemical reasoning such as Cannizaro's proof of the diatomicity of hydrogen (see p. 11) or it can be obtained by measuring the specific heats of the elementary gas at constant pressure and constant volume.

If C_p and C_v stand for the molar specific heats measured in calories at constant pressure and constant volume respectively,

$$C_p = C_v + p\delta v \tag{6.1}$$

where δv is the small increase in volume when the temperature is raised one degree at constant pressure. Applying the gas law,

$$p(v+\delta v) = R(T+\delta T)$$

and hence
$$p\delta v = R\delta T$$

and
$$C_p = C_v + R\delta T$$

Since $\delta T = 1$,

$$C_p = C_v + R \tag{6.2}$$

From the kinetic theory of gases

$$pv = \tfrac{1}{3}Nm\overline{u^2} \tag{6.3}$$

where N is the Avogadro number, m the mass of each molecule and $\overline{u^2}$ the mean square molecular velocity. The kinetic energy per mole is

$$\tfrac{1}{2}Nm\overline{u^2} \tag{6.4}$$

which is clearly equal to $\frac{3}{2}RT$.

The increase in kinetic energy per degree $= \frac{3}{2}R$ which is 3 cal, and this is equal to C_v for a monatomic gas, since a monatomic gas has only 3 degrees of freedom and therefore can only possess kinetic energy. The ratio of C_p/C_v for a monatomic gas must therefore be $\frac{5}{3} = 1{\cdot}67$. All the noble gases and mercury vapour have this value. Polyatomic gases can have additional degrees of freedom such as rotation and vibration. Vibrational energy only becomes significant at high temperatures. A diatomic molecule can rotate about three mutually perpendicular axes, but the moment of inertia about the line joining the two atoms is negligible. In effect the diatomic molecule has two additional degrees of freedom apart from vibration. By the law of equipartition of energy, i.e. that the energy must be equally distributed between the different degrees of freedom, the value of C_p and C_v should be 7 and 5 respectively and the ratio $C_p/C_v = \frac{7}{5}$, i.e. 1·4. The values of C_p/C_v for hydrogen, oxygen, nitrogen and the halogens are very near to 1·4. As the complexity of the molecule increases so the ratio C_p/C_v becomes more nearly equal to 1. The value for turpentine, $C_{10}H_{16}$ is 1·03. The physical method of measuring atomicity is a valuable check on that deduced from chemical reactions.

REGNAULT'S MEASUREMENT OF GAS DENSITY

The first reliable measurements of gas density were carried out by Regnault about 1820. Regnault used two glass globes suspended from the beam of a balance. The volume of each globe was about 50 l. One globe was used as a counterpoise while the other was evacuated, filled with dried air, again evacuated and weighed. It was then filled with the required gas at a known temperature and pressure and re-weighed. The experiment was repeated with hydrogen.

Regnault's original work did not allow for a slight shrinkage which takes place when the globe is evacuated and this shrinkage reduces the buoyancy, increasing the weight of the empty globe. Many years later Lord Rayleigh repeated Regnault's work and was able to measure the shrinkage by immersing the globe in a closed vessel full of water and detecting the change in volume with a capillary tube fitted to the vessel.

The vapour density of the gas was determined by comparing the weight of the globe full of the gas to the weight full of hydrogen, which was taken as the standard gas at that time. When the absolute density was required the globe was weighed filled with water at a known temperature. The method is reasonably accurate but extremely tedious, and modern work uses a quartz fibre buoyancy balance.

THE BUOYANCY BALANCE

The principle of this method, which was developed by Whytlaw-Gray, depends on the determination of the pressures at which the gas in question produces the same buoyancy as a standard gas such as oxygen. The apparatus is illustrated diagramatically in Fig. 6.3.

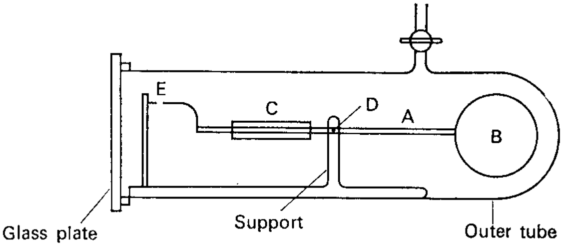

FIG. 6.3. Quartz buoyancy balance.

It consists of a light quartz bulb *B* fixed to a quartz balance beam *A* to which is attached a quartz counterpoise *C* of the same surface area as *B*. The beam turns about a quartz fibre *D*. The whole apparatus can be immersed in a thermostat. The outer tube is first evacuated as completely as possible and then the gas admitted until the beam balances about the zero mark *E*. The pressure is recorded. The gas is then pumped out and oxygen admitted until the balance is again at zero, the pressure of the oxygen being measured. Since the buoyancy exerted by the gas is directly proportional to the density, it follows that

$$\frac{D_1}{D} = \frac{p}{p_1} \tag{6.5}$$

or
$$D_1 = \frac{Dp}{p_1} \tag{6.6}$$

where D_1 and D are the densities of the gas and oxygen and p_1 and p are the corresponding pressures. By suitably loading the beam with weights it is possible to carry out the density measurements over a range of pressures and to extrapolate to zero pressure to correct for deviations from the gas laws (see expt. 6.1). Results of great precision can be obtained with this apparatus since the pressures can be determined, using a suitable manometer, to one part in 100,000. In addition only small volumes of gas are required. The capacity of the outer tube is generally about 25 cc. Adsorption errors are eliminated because the surface area of the buoyancy bulb and the counterpoise are made equal.

A buoyancy balance was used by Whytlaw-Gray in 1933 to carry out a very important piece of work. This consisted in the determination of the atomic weight of carbon by measuring the vapour densities of carbon monoxide, carbon dioxide and ethylene against oxygen. The chemical atomic weight of carbon then in use was 12·00. This disagreed with measurements made with the mass spectrometer which indicated that carbon contained 1% of the ^{13}C isotope. Whytlaw-Gray obtained the value 12·0108 which was in close agreement with the value obtained from the mass spectrometer.

THE MICRO-BALANCE

One of the earliest and most remarkable uses of this type of instrument was the determination of the atomic weight of radon by Ramsay and Whytlaw-Gray. This classical research involved the construction of a highly sensitive micro-balance since the volume of radon available for weighing was less than 0·1 mm^3 and weighed less than 1/1000 mg. To obtain an accuracy of 1% the balance must respond to a load of 1/100,000 mg. The design of such a balance was accomplished by Steele and Grant and the one employed for weighing the radon was a modification. The principle is shown in Fig. 6.4. The balance was constructed of fine quartz fibre. The central knife edge was ground on the end of a quartz rod and rested on a plate of ground and polished quartz crystal supported on the central pillar *A*. The length of the balance arm was 5 cm and the knife edge 1 mm. A concave quartz mirror (not shown) was attached to the beam with a suitable counterpoise and the movement of the beam was observed by reading the position of the image of the filament of a lamp cast on a millimetre scale by the quartz mirror. A small quartz bulb *B* of internal volume about 0·01 cc containing air at a known temperature and pressure was sealed to one end of the balance beam and a small quartz counterpoise *C* was attached to the other end below which was the quartz scale pan *D* to hold the object to be weighed. Final adjustment of the centre of gravity of the beam was made by heating the point of *C* in an oxy-coal gas flame which volatilised minute portions of the quartz. The total weight of the beam with attached mirror, bulb and counterpoise was less than 0·2 g. The whole balance was enclosed in a vacuum-tight case and a thermometer (not shown) was also fixed into the case. A suitable device could raise and lower the knife edge.

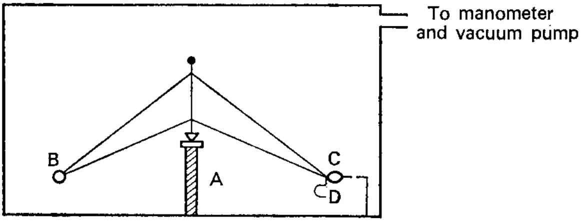

FIG. 6.4. Micro-balance.

The principle of weighing is as follows: with the temperature and pressure in the balance case the same as the temperature and pressure of the air in the bulb *B* the effective weight of this bulb is zero. When the air pressure is reduced the effective weight of the bulb increases, the increase in weight being inversely proportional to the pressure. With this apparatus a change of pressure of 1 mm of mercury corresponds to a change in weight of 1/100,000 mg. The weight of the object in the scale pan is measured by observing the pressure on the manometer when the image of the filament cast by the mirror rests at the predetermined zero.

The radon for this experiment was obtained from a solution of radium bromide and the maximum quantity collected was 0·127 mm^3. This contained traces of hydrogen which had to be removed by freezing the radon in liquid air and pumping off the hydrogen. Some radon was lost in the process. Further corrections had to be made for the loss of radon by decay, and for helium produced during the decay; radon has a half-life of about 4 days (see *Nuclear and Radiochemistry* in this series). The mean of five determinations gave an atomic weight of 223. Since the atomic weight of radium is 226 and radon is formed from radium by the loss of one helium nucleus of mass 4, the atomic weight of radon should be 222. When the extremely small quantity of radon available for the determination is considered the accuracy of Ramsay and Whytlaw-Gray's work is quite remarkable.

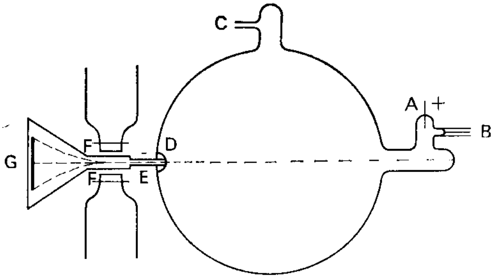

FIG. 6.5. Positive ray analysis tube.

POSITIVE RAY ANALYSIS

The first apparatus was designed by Sir J. J. Thomson in 1910. Thomson's work will now be described. Positive ions were produced in a large highly evacuated bulb (Fig. 6.5), similar to an X-ray tube, the anode *A* being housed for convenience in a side tube. A stream of the gas under investigation was admitted through a very fine bore capillary tube *B* and after circulating through the bulb was pumped off at *C*. The accelerating potential between anode and cathode was about 50,000 V. The cathode *D*, which was hemispherical and made of aluminium, had a hole in it and the positive ions passing through the cathode continued through a very fine bore brass tube *E* and then passed between soft iron pole pieces *FF* placed between the poles of a powerful electromagnet. The pole pieces were insulated from the electromagnet and so could be raised to any suitable potential and used to apply an electric field parallel to the magnetic field. After passing through the electric and magnetic fields the ions impinged on the photographic plate or fluorescent screen *G*. It will be noted that the arrangement was essentially different from the apparatus used to determine *e*/*m* for the electron, in that the fields were applied in the same direction and not at right angles (see Fig. 3.2, p. 34). Unlike electrons, positive ions are produced at different points in the tube and so vary in velocity even when they are all of the same mass. For this reason the action of electric and magnetic fields does not produce a single spot but a line.

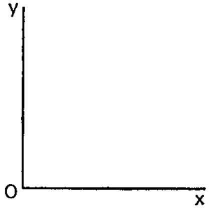

FIG. 6.6.

Consider a positive ion moving perpendicular to the plane of the paper along a line through *O* (Fig. 6.6). If there is no field between the plates *FF* the ion will strike the photographic plate at the spot *O*. If an electric field of strength X e.m.u./cm is now applied in the plane of the paper along the line *Ox* the force on the ion will be Xe dynes, where e is the charge on the ion measured in e.m.u. The kinetic energy of the ion is $\frac{1}{2}mv^2$, where m is the mass and v is the velocity in centimetres per second. Let x be the deflection production. Then clearly

$$x = k_1 \frac{Xe}{mv^2} \tag{6.7}$$

where k_1 is a constant of the apparatus. If the electric field is switched off and the magnetic field applied in the same direction as the electric field similar reasoning to that given on page 33 for the deflection of the electron shows that

$$Bev = \frac{mv^2}{r} \tag{6.8}$$

and so

$$\frac{1}{r} = \frac{Be}{mv} \tag{6.9}$$

where B is the field strength in gauss and r is the radius of curvature of the path of the ion in the magnetic field. If y is the deflection produced simple geometry shows that $y \propto (1/r)$ and

$$y = k_2 \frac{Be}{mv} \tag{6.10}$$

where k_2 is another constant of the apparatus.

By combining the two equations,

$$\frac{y}{x} = \frac{k_2}{k_1} \frac{B}{X} v$$

and

$$\frac{y^2}{x} = k \frac{B^2}{X} \frac{e}{m} \tag{6.11}$$

When both electric and magnetic fields are simultaneously applied and of constant strength, the displacements x and y depend on the velocity of the particle. y^2/x is, however, the equation to a parabola and hence all particles with a constant value of e/m but variable velocity will fall on the plate so as to trace out the path of a parabola (Fig. 6.7). Ions with different values of e/m will form different parabolas.

In practice the magnetic field is reversed and a second exposure made in the same plate in order to determine the position of the line *Ox*. Since $y^2 \alpha (1/m)$ it follows that

$$\frac{y_1^2}{y_2^2} = \frac{m_2}{m_1} \qquad (6.12)$$

and by measuring the values of the vertical displacements it is possible to compare directly the masses of positive ions carrying the same charge. To obtain accurate values for the masses of the positive ions it is necessary to introduce an element of known mass into the discharge tube.

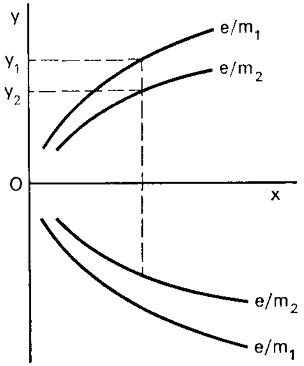

FIG. 6.7.

Apart from parabolas produced by positive ions with a single charge, additional parabolas will be formed by ions carrying two or more positive charges. Most elements do not lose more than two electrons in the discharge tube, but some can lose three or even more and mercury can lose up to eight, thus giving rise to eight parabolas. Even negatively charged ions can be formed which give rise to deflections in the opposite quadrant. For these reasons the interpretations of the tracks produced on the photographic plate are difficult.

One of the most interesting observations made with Thomson's positive ray apparatus was the identification of a parabola corresponding to an atomic weight of 22, using a sample of the lighter constituents of air. At first he thought this line was caused by a doubly charged carbon dioxide molecule which would form a parabola corresponding to a mass of 22, since he had also identified a line corresponding to a mass of 44. However, when the gas entering the tube was passed through liquid air the line corresponding to mass 44 disappeared showing the removal of carbon dioxide, but the 22 line remained. He also noticed that the brightness of the 22 line though considerably fainter than the 20 line corresponding to neon, was roughly proportional to its intensity, i.e. as the 20 line became brighter so did the 22. Thomson concluded that this line was formed either by an unknown element adjacent to neon in the periodic table, or by a compound of neon with hydrogen of formula NeH_2. These observations were made in 1912. At this time the theory of isotopes was in its infancy and had only been proved in the case of radioactive elements. There was no evidence that the stable elements were mixtures of isotopes. Thomson had, in fact, submitted chlorine to positive ray analysis and concluded that it was homogeneous.

THE MASS SPECTROGRAPH

The parabola method for the direct comparison of atomic masses has a limited resolving power. To increase this it is necessary to reduce the thickness of the lines which results in a considerable loss of intensity. In 1919 F. W. Aston devised a type of apparatus which enabled positive ions of different velocities, but of constant e/m to be brought to a focus on a photographic plate. The principle of the method is illustrated in Fig. 6.8. The beam of positive ions passing through the cathode is collimated into a thin ribbon by the slits S_1 and S_2 and spread out into an electric spectrum in the electric field caused by the plates P^+ and P^-. A group of these ions is selected by the slit S_3 and passes between the pole pieces of the powerful electromagnet M. The magnetic field is at right angles to the electric field and its direction set to produce a deflection opposite to the electric field. The photographic plate P is so placed that ions of constant e/m but variable velocity are brought to a focus. With the aid of this apparatus Aston was able to show that neon, chlorine and many other elements were in fact mixtures of isotopes with masses which were, to a close approximation, integral whole numbers. Aston produced an improved apparatus in 1925 capable of estimating the masses of isotopes to 1 part in 10,000. The results of his work are discussed on page 117.

Other forms of mass spectrograph have been devised. A. J. Dempster's model, strictly a mass spectrometer,* uses ions of virtually constant initial velocity. The ions, produced by volatilising a salt placed in a hollow in the anode, or by bombardment with electrons of low velocity, are passed through an electric field, being accelerated by a potential of 1000 V. Their kinetic energy is given by the equation

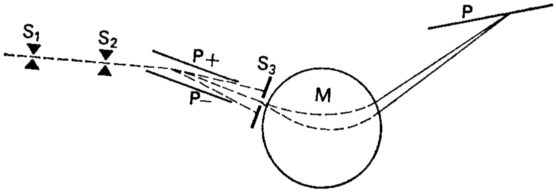

FIG. 6.8. Aston's mass spectrograph.

$$Ve = \tfrac{1}{2}mv^2 \tag{6.13}$$

V being the accelerating potential and e the charge on the ion both being measured in e.m.u. The principle is analogous to the determination of e/m for the electron (see p. 33) since ions with a given value of e/m are of virtually constant velocity. The ions are passed through a slit and bent into a semicircle by a powerful magnetic field (Fig. 6.9), and after passing through another slit fall

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* The term " mass spectrograph " strictly applies to an instrument which produces lines on a photographic plate. Ion collecting devices are more properly called " mass spectrometers ".

on an ion collecting device. Thus

$$\frac{e}{m} = \frac{v}{Br} \tag{6.14}$$

(eqn. (3.2), p. 33).
From eqn. (6.13)

$$v^2 = 2V\frac{e}{m} \tag{6.15}$$

Squaring eqn. (6.14) gives

$$v^2 = \frac{e^2}{m^2}B^2r^2 \tag{6.16}$$

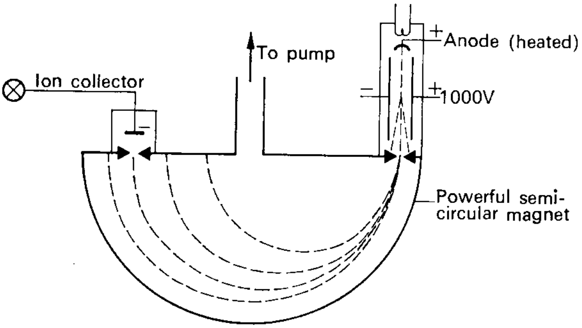


FIG. 6.9. Dempster's mass spectrograph.

Hence, by combining eqns. (6.15) and (6.16) to eliminate v^2,

$$\frac{e}{m} = \frac{2V}{B^2r^2} \tag{6.17}$$

In practice B is kept constant and V is varied. The method is called " direction focusing " since ions having slightly different directions but the same values of e/m are brought to the same focus by the 180° magnetic field.

A third type of mass spectrograph, produced by Bainbridge in 1930, is a modification of Dempster's model and uses the principle known as velocity focusing. The ions produced from a heated anode or ordinary discharge tube are first collimated and then passed through opposed electric and magnetic fields in an arrangement similar to that used in Thomson's method for the determination of e/m for the electron. This arrangement acts as a velocity selector and ions which pass through undeflected all have identical velocities irrespective of the value of e/m since $v = X/B_1$ (see eqn. (3.4), p. 35), where v is the velocity of the ions, X the electric field strength, and B_1 the magnetic field strength, both field strengths being maintained constant. After traversing the velocity selector they enter a very powerful magnetic field as in Dempster's apparatus and are bent into a semicircle. The radius of this semicircle $r = mv/B_2e$ (eqn. (6.9)), where B_2 is the strength of the second magnetic field. Since v, B_2 and e are constant, r is proportional to m and a linear mass scale is produced on the photographic plate.

Modern types of mass spectrograph, more properly called mass spectrometers, use ion collecting devices and after suitable amplification the currents produced can be traced on a paper recorder. The positive ions are produced by electron bombardment and are of low, approximately constant velocity. In the simpler type of instrument the ions are collimated and are passed through a magnetic field arranged to give a 90° deflection before falling on the ion collector. Such instruments are much used in routine chemical analysis of gaseous mixtures, but the resolution is limited. Simple molecules form charged radicles due to the electron bombardment so their masses may be detected and their proportion determined. More complex molecules break down, but they give a characteristic " cracking pattern " from which they can be identified. Mass spectrometers can be used to help in the determination of the structure of complex molecules by identifying the charged fragments produced on electron bombardment.

The modern high resolution mass spectrometers pass the ions first through an electric field where they are accelerated to a constant velocity before being collimated and submitted to a very powerful magnetic field, also arranged to give a 90° deflection. These instruments can even distinguish between such species as

N_2^+, CO^+ and $C_2H_4^+$ with masses in a.m.u. (atomic mass units) of 28·0061, 27·9949 and 28·0313, respectively. They can also be used for determining atomic weights on the chemical scale, now based on $^{12}C = 12{\cdot}0000$, and the masses of the isotopes and the proportions of each isotope present can be measured with such a high degree of precision that the results in most cases are equal to if not better than the best values obtained by chemical analysis.

THE PACKING FRACTION

Aston proved the existence of isotopes of the non-radioactive elements with the aid of his first mass spectrograph and showed that the masses were very approximately whole numbers. This recalls the hypothesis of Prout in 1815 that all elements were composed of hydrogen. The hypothesis was rejected early in the nineteenth century since chemical atomic weights were soon shown to depart from the whole number rule. With the discovery of isotopes the hypothesis was revived and is now accepted in a modified form, i.e. that the nuclei of all elements are composed of protons and neutrons. In consequence the isotopic masses should be slightly greater than whole numbers since the mass of a proton is 1·0076 and a neutron 1·0090 compared to the isotope of oxygen $^{16}O = 16{\cdot}0000$. The isotopic mass is the mass of the nucleus added to the masses of the electrons which make up the neutral atom. With increase in atomic weight the departure from the whole number rule should increase progressively.

With improvement in resolution, divergence from the whole number rule could be measured and after the construction of his second mass spectrograph in 1925 Aston was able to show that the isotopic masses first *decreased* sharply, reaching a minimum about iron and then gradually increased. He defined this " loss of mass " as a " packing fraction " which was expressed as:

$$\frac{\text{isotopic mass—mass number}}{\text{mass number}} \times 10^4$$

the mass number being the isotopic mass expressed on the ^{16}O scale rounded off to a whole number.

If the packing fractions are plotted against the mass number, the curve shown in Fig. 6.10 is obtained. The packing fraction is clearly related to nuclear stability. Nuclei with positive packing fractions must be relatively unstable while those with negative packing fractions must be relatively stable. The minimum in the packing fraction curve occurs around iron, cobalt and nickel and this accounts for the preponderance of these elements in the core of the earth. It will be noticed that the packing fraction becomes positive again at mass number 200 corresponding to mercury. All elements beyond mercury have natural radioactive isotopes showing that their nuclei can decompose spontaneously.

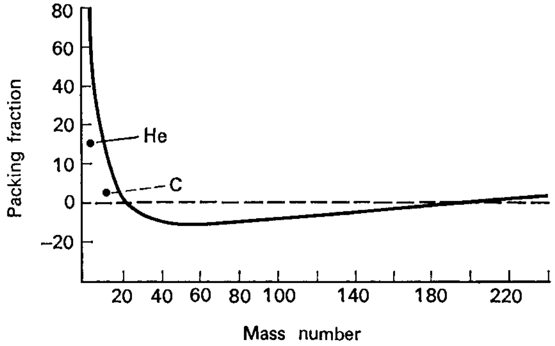


FIG. 6.10. Packing Fraction Curve.

NUCLEAR BINDING ENERGY

The masses of the individual nucleons which make up the nucleus are together greater than the observed mass of the nucleus itself. This difference is referred to as the " mass defect ". An example will make this clear. Consider the α-particle of mass number 4. It consists of two protons and two neutrons. The mass of a single proton is 1·0076 nuclear mass units (n.m.u.) and that of a neutron is 1·0090 n.m.u. (The n.m.u. is defined as one-twelfth of the mass of the ^{12}C nucleus and is equal to $1{\cdot}66 \times 10^{-24}$ g.) The combined masses of the four independent nucleons is 4·0332, but the actual mass of the α-particle is 4·0017 n.m.u. The mass defect is therefore 0·0315 n.m.u. This quantity can be expressed in energy units by use of Einstein's relativity equation $E = mc^2$, where c is the velocity of light. Applying this to the mass defect of the α-particle gives

$$E = 0{\cdot}0315 \times (2.99 \times 10^{10})^2$$

$$= 2{\cdot}82 \times 10^{19} \text{ ergs/g atom,}$$

which is equivalent to

$$\frac{2{\cdot}82 \times 10^{19}}{6{\cdot}023 \times 10^{23} \times 1{\cdot}60 \times 10^{-6}}$$

$$= 29{\cdot}2 \text{ MeV per nucleus}$$

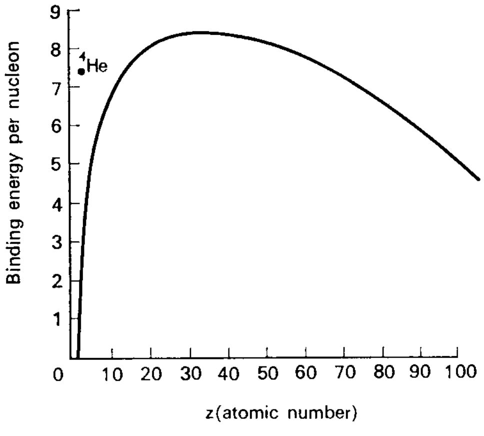


FIG. 6.11. Binding energy.

This represents the total nuclear binding energy. The binding energy of any atomic nucleus can be calculated in a similar way.

The stability of nuclei can be expressed most clearly in terms of binding energy per nucleon. To obtain this quantity the total binding energy is divided by the mass number. The α-particle has a binding energy of 7·3 MeV per nucleon. The curve shown in Fig.

6.11 shows how the binding energy varies with the mass number. Those nuclides which lie above the curve show exceptional stability. It will be seen that nuclear energy can be released either by the fission of heavy nuclei to form two lighter nuclei or by the fusion of light nuclei to produce heavier nuclei. These processes have been demonstrated spectacularly in the explosion of uranium and hydrogen bombs. (The stability of nuclei is discussed in greater detail in volume 2.)

Chemical methods of determining atomic weights

The first table of atomic weights was produced by Berzelius as explained on page 9. He determined his atomic weights through equivalents using such methods as direct conversion to an oxide, reduction of an oxide by hydrogen, indirect conversion to an oxide using nitric acid and displacement of hydrogen from an acid. He based his equivalents on O = 100 as a standard and subsequently changed this to H = 1. His methods of analysis were a great advance on previous work, but his theoretical basis for fixing the correct values of the atomic weights was unsound.

An accurate value for the ratio hydrogen : oxygen was essential and this measurement was carried out by Dumas in 1842 (Fig. 6.12). Considering the difficulties under which he worked, the result was remarkably accurate. He had no corks or rubber tubing and had to make all his joints with oiled silk tied with cotton. As a mean of nineteen experiments extending over 9 months, he obtained a ratio of hydrogen to oxygen of 1 : 7·98 or 1·002 : 8·000. This value for the equivalent of hydrogen is slightly low, probably because his copper oxide was not perfectly dry. The copper formed also adsorbs some hydrogen. In addition the hydrogen was slightly contaminated with sulphur dioxide due to reduction of the concentrated sulphuric acid drying agent by the hydrogen.

Fifty years later the gravimetric analysis of water was repeated by Morley (1896) (Fig. 6.13). This classical research has been described as one of the most accurate experiments ever to be

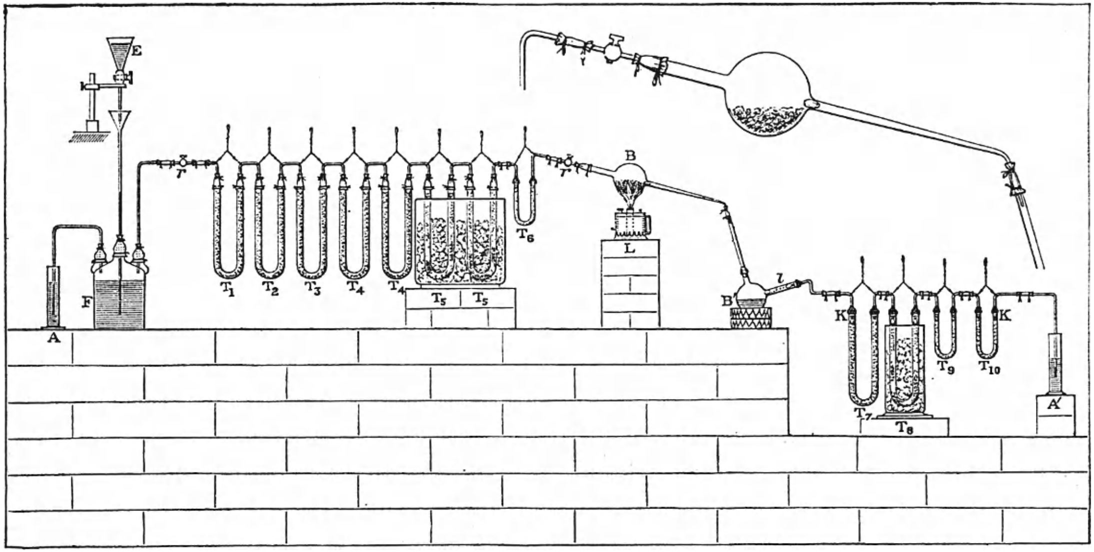


Fig. 6.12. Dumas's apparatus for determining the composition of water. The insert shows the copper oxide bulb on a larger scale. The details of the apparatus are as follows: *F*, flask for generating hydrogen; *E*, tap-funnel containing sulphuric acid; *A*, safety-valve of mercury; T_1, tube containing glass moistened with lead nitrate; T_2, tube containing glass moistened with silver sulphate; T_3, tube containing (*a*) alkaline pumice, (*b*) solid potash; T_4T_4, ignited potash, broken; T_5T_5, tubes containing pumice coated with phosphoric anhydride and cooled with a freezing mixture; T_6, guard tube containing pumice and phosphoric anhydride; *B*, bulb containing copper oxide, with tap above, and pointed beak below to carry off water; *L*, spirit lamp; *B*, receiver for water, with fragments of calcium chloride at *l*; T_7, ignited potash; T_8, phosphoric anhydride in a freezing mixture; T_9, guard tube containing phosphoric anhydride; T_{10}, phosphoric oxide (not weighed) to exclude moisture; *A*, valve containing sulphuric acid, for escape of hydrogen.

performed. The weakness of Dumas's technique lay in his determination of the weight of hydrogen by the difference between the weight of water formed and the loss in weight of the copper oxide. Thus all the error of the process was accumulated upon the measurement of the hydrogen, the smallest weight to be determined. Morley used instead the direct synthesis of water from known weights of hydrogen and oxygen contained in glass globes. The hydrogen was prepared by the electrolysis of dilute sulphuric acid and purified by passing over heated copper to remove traces

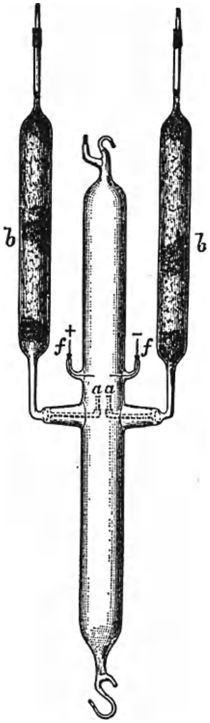


FIG 6.13. Morley's combustion-tube. The gases were admitted by jets *aa* after passing through drying tubes *bb*; they were ignited by sparking *ff*.

of oxygen, through alkali to remove acid gases, dried with phosphorus pentoxide and finally occluded by palladium, one volume of which can absorb 900 vol of hydrogen; palladium does not absorb other gases. The hydrogen was released by heating the palladium. Pure oxygen was prepared by heating potassium chlorate alone.

The apparatus was evacuated and weighed and then the hydrogen and oxygen were burnt at the platinum jets with oxygen in slight excess; the water formed condensed in the bottom of the apparatus. When a suitable amount had been collected the lower tube was immersed in a freezing mixture, and the apparatus once more evacuated and weighed, any water vapour being collected in the phosphorus pentoxide drying tubes. This gave the weight of water formed. The residual gas was analysed and the globes containing the hydrogen and oxygen were also re-weighed. The loss in weight of the two globes, together with the analysis of the residual gas, enabled the combining ratio of hydrogen to oxygen to be calculated. The weight of the water formed was found to be exactly equal to the loss in weight of the two globes. The result obtained was 1·0076 : 8·0000.

THE WORK OF J. S. STAS

Stas, a former pupil of Dumas, carried out the most accurate determinations of atomic weights performed in the nineteenth century. As a result of the work of Cannizao approximate values for atomic weights were known and the formulae of most inorganic compounds could be fixed with certainty. The problem was to determine precise values of atomic weights. Stas realised that the key to the problem was the atomic weight of silver, since the chlorides or bromides of nearly every metal could be prepared by recrystallization or sublimation in a very pure state and then precipitated as silver chloride or bromide. $O = 16{\cdot}000$ was taken as the standard, but the direct ratio of silver to oxygen could not be determined since the oxides of silver are too unstable. Stas therefore determined the ratio $3O : KCl$ by decomposition of potassium chlorate followed by the ratio KCl : Ag. Hence

$$\frac{3\,\mathrm{O}}{\mathrm{KCl}} \cdot \frac{\mathrm{KCl}}{\mathrm{Ag}} = \frac{3\,\mathrm{O}}{\mathrm{Ag}}$$

The determination of the first of these ratios is a matter of some difficulty. When potassium chlorate is heated, very fine particles of potassium chloride are carried away by the stream of oxygen and elaborate precautions must be taken to trap these particles. If manganese dioxide is added the decomposition proceeds much more smoothly, but side reactions occur with some loss of chlorine.

Stas worked with very large quantities of material, hoping thereby to increase the accuracy of his results. He often used as much as 400 g of silver in a single experiment. Unfortunately, his silver has been shown to contain at least 0·015% of oxygen since it was fused in an oxidising atmosphere. He poured the molten metal into cold water to produce fine pellets and the sudden cooling prevented the liberation of the trapped oxygen. His value for the atomic weight of silver of 107·93 was therefore too high. Other minor errors occurred such as the occlusion of silver nitrate in the silver chloride precipitated and the retention of small quantities of water in his potassium chlorate. Despite these errors there is no doubt that Stas's work was remarkably accurate for his day.

THE WORK OF T. W. RICHARDS

During the years 1900–10 T. W. Richards and his co-workers, working at Harvard, carried out the most accurate chemical determinations of atomic weights which have at present been performed. Richards realised that one serious error occurring in Stas's work was the occlusion of water in his potassium chlorate. To remove water it is necessary to fuse the substance. Potassium chlorate loses some oxygen on fusion and, as mentioned previously, it is most difficult to trap the fine particles of potassium chloride which are given off during the decomposition. Richards obtained the ratio of silver to oxygen by use of lithium perchlorate. This substance fuses at 230°C and does not lose oxygen at 300°C. It has a very high proportion of oxygen by weight and can be readily purified. Unfortunately, it is impossible to determine the ratio $LiCl : 4\,O$ by direct decomposition since very fine particles of lithium chloride are ejected and will colour a flame 15 ft distant if the reaction is performed in an open dish. He therefore decided to work by synthesis. Very pure lithium chloride was converted to the perchlorate by evaporation with a slight excess of perchloric acid. The resultant lithium perchlorate was fused in dry air and allowed to solidify slowly. A glass-like solid was obtained free from water and adsorbed air. By these means he obtained the ratio $LiCl : 4\,O$.

He then determined the ratio $LiCl : Ag$. The silver was obtained from purified silver nitrate by reduction with ammonium formate and fusion in a current of hydrogen, thus avoiding the occlusion of oxygen as occurred in Stas's work. Lithium chloride was purified and fused in a current of dry hydrogen chloride and nitrogen. The pure lithium chloride was dissolved in water and the calculated quantity of silver dissolved in dilute nitric acid was added followed by a slight excess of silver nitrate to complete the precipitation of the silver chloride. This greatly diminished the danger of occlusion of silver nitrate in the precipitated silver chloride, which was one of Stas's errors. The excess silver in the filtrate was determined and the whole operation was performed in a red light to prevent photochemical reduction of the silver chloride. The silver chloride was washed ten times with dilute nitric acid cooled in ice, fused and weighed. The washings were collected and a small known weight of silver nitrate added. This produced an opalescence. This opalescence was compared in a nephelometer with that produced by using a solution containing a known weight of silver chloride which had been similarly treated with the same known weight of silver nitrate. By this means Richards was able to correct for the weight of silver chloride lost in the washings. He obtained the value of 107·871 for the atomic weight of silver and 6·9401 for the atomic weight of lithium in terms of $O = 16{\cdot}0000$.

Another method used was to determine the ratio $I_2O_5 : 2Ag$. Purified iodic acid was dehydrated at 240°C and the iodine pentoxide weighed. This was dissolved in dilute nitric acid, reduced to iodide with hydrazine and precipitated as silver iodide by adding a known weight of silver as nitrate in slight excess. The excess silver was determined. This gave the atomic weight of silver as 107·864.

Finally, the determination of the ratios

$$AgNO_3 : Ag,\ NH_4Cl : AgCl \text{ and } Ag : AgCl$$

must be mentioned. The first ratio was determined both by thermal decomposition of silver nitrate and by synthesis from silver. Six determinations differed by less than 1 part in 100,000. For the measurement of the second ratio the ammonium chloride was first sublimed in a current of ammonia and then *in vacuo*, being weighed in an evacuated weighing bottle. The ammonium chloride was converted to silver chloride exactly as in the case of lithium chloride (p. 125). The third ratio had already been determined under the ratio $LiCl : Ag$ since the exact weight of silver reacting with lithium chloride was known and also the weight of silver chloride produced. By carrying out the precipitation of silver chloride with an excess of silver rather than chloride any loss of silver chloride as the complex $AgCl_2^-$ was prevented. From these measurements the atomic weights of silver, nitrogen and chlorine can all be calculated, assuming the atomic weight of hydrogen (see expt. 6.2). The atomic weight of silver as determined by this method was found to be 107·880.

Following up this work, Richards carried out the exact measurement of the equivalent weights of some twenty-two other elements, mostly by the conversion of the chlorides or bromides to the corresponding silver salt. His work was marked by a refusal to take anything for granted. In his own words he said: " All liquids tend to dissolve something from every other phase, solid, liquid or gas, with which they come in contact. Every substance separating as a new solid phase tends to retain upon itself or within itself some of the other substances in the phase from which it separated." No student of analysis could do better than to read his paper: *Methods used in Precise Chemical Investigation*, Carnegie Publication 125, 1910, p. 97.

EXPERIMENTS

6.1. CONSTRUCTION AND USE OF A BUOYANCY BALANCE

The construction of a quartz buoyancy balance is a difficult and delicate operation requiring the services of an expert glass-blower and special equipment. A simple alternative is to build one in pyrex glass (Fig. 6.14). First blow a light bulb about 3 cm in diameter and attach this to a thin glass rod about 0·5 mm in diameter and 15 cm long. Attach three thin microscope cover slips, 2 cm square, with Araldite, to the rod about 1–2 cm from the

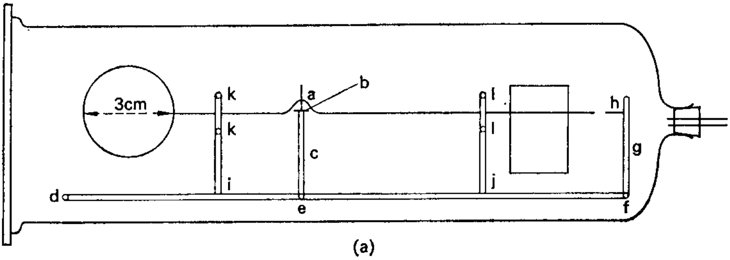


FIG. 6.14(*a*). Buoyancy balance in bell jar (side elevation).

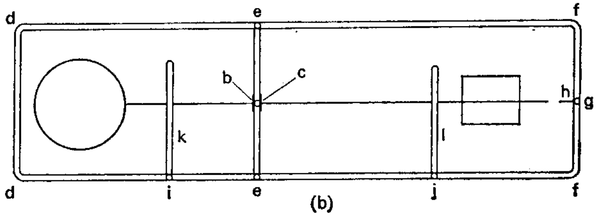


FIG. 6.14(*b*). Buoyancy balance (plan showing framework).

end. These should be fixed approximately at 120°. Their function is to allow for adsorption on the surface of the bulb. With a bulb of 3 cm diameter their combined surface area will be approximately equal to the surface area of the bulb.

Determine the approximate centre of gravity of the beam and make a bend as shown at *a*. To bend such a thin rod it is necessary to use a very small flame. A convenient flame size can be obtained by using a hypodermic needle cut off square. Attach a very thin glass rod about 1 cm long to the top of the bend at *a*. Break off a small piece of razor blade about 0·5 cm long and 2–3 mm wide and attach this to the bend with Araldite, having the sharp end down. Cut a small piece of glass about 1 cm by 0·4 cm off a microscope slide and secure this, *b*, to the end of a glass rod *c* with Araldite. This serves as the plane on which the razor blade will pivot.

Make a light frame of glass rod about 1 cm longer than the beam, joined horizontally with three glass rods *dd*, *ee*, *ff*. Attach *c* to the middle of *ee* so that it is vertical and the plane horizontal. It may be more convenient to fix the plane *b* after the rod *c* has been attached to *ee*. Join another glass rod *g* vertically to the mid-point of *ff* and attach a small pointed rod *h* to *g* to indicate when the beam is horizontal. Lastly, fix two more glass rods at *i* and *j* and attach to each two horizontal rods *kk* and *ll*. These serve to prevent the balance from swinging too far; they can also be used to support the beam when it is not resting on the plane. The whole apparatus should be slid into a small glass bell jar with a ground glass flange. The top of the bell jar is closed with a one-holed rubber bung carrying a glass tube with a tap which can be connected with pressure tubing to a vacuum line.

The sensitivity of the balance will depend on the position of the centre of gravity of the beam and the weight of the beam. The centre of gravity should be about 0·2 mm below the knife edge and slightly to the right (Fig. 6.14a) so that the bulb is " light " at atmospheric pressure in air. The height of the centre of gravity can be adjusted by bending the beam slightly or by drawing small pieces of glass off the light rod attached at *a*. With a bulb of 3 cm diameter the mass of air displaced by the bulb at atmospheric pressure will be about 0·02 g. The bulb should balance when the air pressure inside the case is about 0·5 atm. The simplest way to adjust this is to make a small rider weighing about 0·02 g, hang this on to the beam midway between the knife edge and the centre of the bulb and shorten or lengthen the long arm of the beam until a balance is achieved.

To use the balance a simple vacuum line is required. This should be attached to two storage vessels with well-fitting taps, one to contain nitrogen and the other the experimental gas. Carbon dioxide would be quite suitable. A mechanical pump is advisable, but a water pump could be used. A mercury manometer must be connected to the vacuum line. Both storage vessels are evacuated and one is filled with nitrogen and the other with the gas under test. The buoyancy balance case is then evacuated and nitrogen slowly admitted until a balance is achieved. The manometer is read and the balance and vacuum line again evacuated. The gas under test is then admitted until the balance is horizontal. The second reading of the manometer is taken. From the results the density of the gas is easily determined in terms of nitrogen (see p. 106). The best results will be achieved by using a cathetometer to observe the pointer and to determine the null point.

6.2. DETERMINATION OF THE ATOMIC WEIGHTS OF SILVER, CHLORINE AND NITROGEN BY GRAVIMETRIC ANALYSIS

To carry out this experiment it is necessary to determine three ratios, silver nitrate : silver, silver chloride : silver, and ammonium chloride : silver chloride. The three atomic weights can then be determined assuming the atomic weights of hydrogen and oxygen to be 1·0076 and 16·000 respectively.

(a) Silver nitrate : silver

(i) By decomposition. Weigh into a weighed pyrex test tube approximately 1 g of powdered " analar " silver nitrate which has been dried in an oven at 120°C. Insert a piece of glass wool into the test tube to trap any fine particles which may be carried out during the decomposition, and reweigh. Heat the tube and its contents gently and then more strongly until all traces of brown fumes of nitrogen dioxide have been removed. Cool and reweigh. Repeat to constant weight.

(ii) By synthesis. Weigh approximately 0·5 g of pure silver foil into a weighed 100 ml beaker. Dilute 5 ml of " analar " concentrated nitric acid to 20 ml with good quality demineralised water and pour this on to the foil, covering the beaker with a clock glass. Allow the silver to dissolve slowly. When it has all dissolved, evaporate the solution on a water bath to dryness. Add a little demineralised water and repeat the evaporation. Test the vapour coming from the beaker with litmus. Repeat the evaporation until all traces of acid fumes have been removed. Normally two evaporations to dryness will be sufficient. Finally dry in the oven at 110°C and weigh. Avoid exposing the silver nitrate to bright light if possible.

(*b*) *Silver : silver chloride*

Dissolve the silver nitrate obtained in (*a*) (ii) in about 10 ml of demineralised water in the beaker and add carefully 4 ml of 2M (bench) hydrochloric acid. Stir gently with a small glass rod, washing the end of the rod into the beaker until all traces of silver chloride have been removed. 5 to 10 ml of water should be more than sufficient for washing the rod. Surround the beaker with black paper and place in a cupboard to coagulate the precipitate. Leave for a few hours, preferably overnight.

Weigh a scintered glass crucible filter (porosity No. 4), which should have been dried in an oven. If glass filters are not available use a Gooch crucible and prepare an asbestor filter. Attach the filter with a suitable funnel to a suction flask and transfer the precipitated silver chloride on to the filter by pouring down a glass rod and washing with a jet of distilled water. Inexperienced students should ask for a demonstration and practice this technique before attempting the quantitative transfer of the precipitate. All traces of the precipitate must be removed from the beaker on to the filter. It will be necessary to attach a rubber " policeman " to the end of the glass rod and rub the sides of the beaker, washing the " policeman " into the funnel. Wash the precipitate thoroughly, but use several small washings. The solubility of silver chloride is about 1 mg/l. If less than 100 ml of water are used the error involved will not be detectable on a balance sensitive to 0·1 mg. Finally, wash the silver with a little acetone and dry in the oven at 130°C to constant weight.

(*c*) *Ammonium chloride : silver chloride*

" Analar " ammonium chloride is pure enough for most purposes. If necessary it can be sublimed. For the highest accuracy it should be sublimed in a current of ammonia and finally *in vacuo.*

About 0·5 g of the pure ammonium chloride accurately weighed is dissolved in 5 ml of water. About 2·5 g of pure silver nitrate is dissolved in 10 to 20 ml of water and the solution carefully poured into the solution of ammonium chloride. The precipitated silver chloride is treated exactly as in (*b*) and weighed. For convenience it can be collected and weighed in the glass filter used in (*b*) on top of the previous precipitate. This saves cleaning the filter and reweighing.

Finally, save all silver residues, including the contents of the suction flask used in (*c*) and transfer to the silver residues bottle.

The glass filters are best cleaned by soaking in 0·880 ammonia in the fume cupboard, washing and drying in the oven. If they are still dark this will be due to traces of silver which can be removed with hot concentrated nitric acid.

Calculation of results

$$\frac{\mathrm{AgNO_3}}{\mathrm{Ag}} = a, \qquad \text{(i)}$$

$$\frac{\text{AgCl}}{\text{Ag}} = b, \tag{ii}$$

$$\frac{\text{NH}_4\text{Cl}}{\text{AgCl}} = c. \tag{iii}$$

Let the atomic weights of silver, nitrogen and chlorine be x, y and z respectively.

Then taking H = 1·0076 and O = 16·0000

$$x+y+48 = ax, \tag{iv}$$

$$x+z = bx, \tag{v}$$

$$y+4{\cdot}0304+z = c(x+z). \tag{vi}$$

Substituting in eqn. (vi) the value of y as found from eqn. (iv) and rearranging terms, we have

$$(a-1)x-cx+(1-c)z = 43{\cdot}9696, \tag{vii}$$

but, according to eqn. (v), $z = (b-1)x$.

Hence, substituting for z in (vii) and rearranging terms gives

$$x = \frac{43{\cdot}9696}{a+b-bc-2}$$

(The student should work this out for himself.)

y and z are obtained by substituting in eqns. (iv) and (v).

QUESTIONS

6.1. Define atomic weight and describe briefly one physical and one chemical method for determining this quantity. What connection has the atomic weight of an element with the masses of the atoms of that element? Why do the isotopes of an element have the same chemical properties? [O. & C. G.C.E.]

6.2. Give a brief account of the methods which have been used for the determination of the atomic weights of the elements. [Oxford Prelim.]

6.3. Give a brief historical account of the development of our knowledge of stable isotopes, mentioning the contributions of the more important workers in this field. Show, by reference to examples, how isotopes may be used in elucidating chemical problems. [Imperial College Schol.]

6.4. Define *atomic weight*, *atomic number*, *atomic volume*. Calculate the *accurate* atomic weight of silver from the following data: 0·5000 gm of silver nitrate (the formula is known to be $AgNO_3$) yielded on ignition 0·3170 gm of pure silver. 0·7717 gm of ammonia (the formula is known to be NH_3 and the atomic weight of hydrogen to be 1·008) occupied 1 litre at 760 mm pressure and 0°C. The ratio P_1V_1/P_0V_0 for ammonia is 0·9872, where V_1 is the volume of a given mass of ammonia at a pressure of 1 atmosphere, and V_0 is the volume of the same mass of ammonia when the pressure approaches zero. (O = 15·999, ^{12}C = 12·000.) [Cambridge Schol.]

6.5. Exactly 1 gm of silver was dissolved in nitric acid, and the solution was added to a solution containing 0·4810 gm of potassium chloride, to give 0·9243 gm of silver chloride. When the filtrate was treated with an excess of potassium chloride, 0·4043 gm of silver chloride was obtained. Calculate the combining ratio by weight of potassium and chlorine. [Cambridge Schol.]

6.6. Describe in detail *one accurate* method for the determination of atomic weights. [Oxford Schol.]

APPENDIX 1

TO DETERMINE THE POTENTIAL ENERGY OF AN ELECTRON IN A GIVEN ORBIT OF RADIUS r

THE force of attraction of a proton (hydrogen nucleus) on the electron

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

where e is the charge on the electron and r the distance of the electron from the nucleus.

Let the electron be moved outward a distance dr. Then the work done against the attractive force of the nucleus

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

The work which must be done to transfer the electron to infinity

$$= \int_r^\infty \frac{e^2}{r^2}dr = \frac{e^2}{r}$$

The potential energy is numerically equal to this with the sign changed, i.e.

$$-\frac{e^2}{r}$$

APPENDIX 2

THE MEASUREMENT OF LATTICE SPACING

CONSIDER a parallel beam of X-rays falling on a crystal face at a glancing angle θ (Fig. A.1). Part of the beam represented by AB will be reflected at the surface layer along BC, but other parts represented by DE, FG will penetrate the crystal and be reflected from the successive planes of ions in the lattice, YY, ZZ. If the path length ABC differs from DEC by a whole number of wavelengths, reinforcement will occur and a diffraction image will result. The difference in path length can be calculated as follows: draw BH perpendicular to XX, YY, etc., and BI perpendicular to AB, DH, etc. Clearly the path length of the two rays considered will differ by $EB-EI$, and since $EB = EH$ the differences must be IH. Now $IH = BH \sin\theta = 2d \sin\theta$. Hence the condition for the formation of a diffraction image by X-rays falling on a crystal is

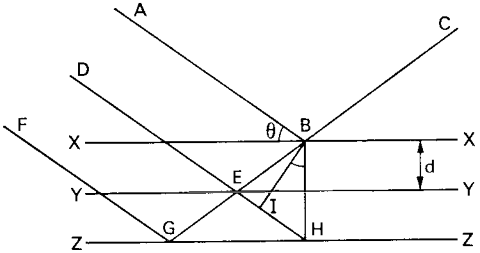


FIG. A.1.

$$n\lambda = 2d \sin\theta$$

where λ is the wavelength of the X-rays and n is an integer. If the beam of X-rays is homogeneous, λ is fixed and as θ is increased a series of diffraction images will be formed corresponding to integral values of n. By measuring θ and knowing λ it is thus possible to determine d, i.e.

$$d = \frac{n\lambda}{2 \sin \theta}.$$

MISCELLANEOUS QUESTIONS

1. Just over a hundred years ago the atomic weight of carbon was thought to be 6 and that of oxygen 8, and the formula for water was written HO. What arguments would you use if you were asked (*a*) why the atomic weight of carbon is now considered to be 12 and not 6, and (*b*) why the formula for water is written H_2O?

   What significance is there in the fact that the atomic weight of carbon is nearer 12·1 than 12? [O. & C. G.C.E.]
2. State the empirical laws of chemical combination and show how apparent anomalies were finally reconciled.

   Give a brief account of the structure of the atom, indicating points of difference between your view and that held a century ago. [Imperial College Schol.]
3. The following names are all associated with one particular aspect of theoretical chemistry: Berzelius, Döbereiner, Dumas, Newlands, Lothar Meyer, Mendele'ef.

   Discuss the development of this aspect in terms of the contributions made by these workers, and mention any later workers whom you consider to have made major advances in this field. [Imperial College Schol.]
4. Show how a knowledge of the electronic structure of the elements leads to an understanding of the main features of the Periodic Table. [Oxford Schol.]
5. What do you understand by a Transition Element? Illustrate the important characteristics of these elements by reference to the chemistry of iron. [Oxford Schol.]
6. Write a short essay on " Isotopes ". [Oxford Schol.]
7. " The valency of an element is a small whole number." Discuss. [Oxford Schol.]
8. " The elements in a group of the periodic classification increase in metallic character in order of increasing atomic weight." Illustrate this statement by considering any one such group. [Oxford Schol.]
9. " Metallic character of the elements in the Periodic Classification decreases in progressing from left to right in the table but increases in progressing from top to bottom." Summarize clearly and concisely in note form what you feel are the key points in favour of or against such a statement, illustrating your answer by carefully chosen examples where possible. [Cambridge Schol.]
10. " Atomic number forms a more satisfactory basis for the classification of the elements than atomic weight." Discuss this statement. [Oxford Schol.]

11. Outline an experiment that you would carry out to determine the atomicity of a simple gaseous molecule, and the theoretical reasoning that you would use in interpreting the result. [Cambridge Schol.]
12. " Boron is classified with aluminium in the same group of the periodic table; it also resembles carbon and silicon." Discuss this statement. [Oxford Schol.]
13. Define *atomic weight* and *atomic number.* Criticise your definitions. Outline the periodic table and insert the first ten elements in their proper places. Relate the position of these elements to the electronic configurations of their atoms. Show how the configuration is related to the oxidation state of the element. Illustrate your answer by reference to NaCl, Cl_2, CO_2 and NH_4Cl.
14. Sketch the general layout of the Periodic Table, and place in their appropriate positions the elements in periods 1, 2 and 3 (hydrogen to argon), the alkali metals and the halogens. Comment on the positions assigned in the Table to hydrogen, the inert gases and the transition elements. [Cambridge Schol.]
15. How were the rare gases discovered? Although these elements are comparatively inert their existence is of great importance in chemical theory. Why is this?
16. Would you advise the adoption of a Chemistry syllabus which began with a treatment of the theories of atomic and molecular structure rather than with the conventional description of inorganic reactions? Illustrate your answer by reference to one group or series of elements of the Periodic Table. [Oxford Schol.]
17. Summarise, and comment briefly on, the chief modifications in the periodic classification of the elements since the time of Mendele'ef. [Oxford Schol.]
18. What do you understand by Avogadro's hypothesis? What are the reasons for our belief in it? What is the relation between Avogadro's Number and the Faraday? [Oxford Prelim.]
19. Explain what you understand by (*a*) atom, (*b*) the periodic classification, (*c*) atomic number.

    Describe briefly, and exemplify, the variation of physical and chemical properties likely to be found among elements in (i) a group, (ii) a period, (iii) a transition series, of the periodic classification. [Cambridge Schol.]

ANSWERS TO NUMERICAL QUESTIONS

Question	*Answer*
1.1	51·0
3.1	$4{\cdot}79 \times 10^{-10}$ e.s.u.
3.3	17·9 cm, 1·33 Oersted
3.4	$1{\cdot}88 \times 10^{8}$ cm sec^{-1}
3.5	48 cm
3.6	$1{\cdot}42 \times 10^{24}$
3.8	9, 7, 6, 5, 8 respectively
3·9	$1{\cdot}18 \times 10^{-4}$ cm
4.1	13·4 eV
4.3	(*b*) $6{\cdot}81 \times 10^{-27}$ erg sec
4.4	$6{\cdot}59 \times 10^{-27}$ erg sec
4.5	$5{\cdot}51 \times 10^{-12}$ cm
5.4	$2{\cdot}9 \times 10^{10}$ per cent
5.5	298, 124, 400 kcal respectively
6.4	107·4
6.5	K : Cl = 1·103 : 1

THE ELEMENTS ARRANGED IN ALPHABETICAL ORDER OF THEIR CHEMICAL SYMBOL

Symbol	*Name*	*Atomic Number*	*Atomic Weight*
A or Ar	Argon	18	39·944
Ac	Actinium	89	227
Ag	Silver	47	107·880
Al	Aluminium	13	26·98
Am	Americium	95	(243)
As	Arsenic	33	74·91
At	Astatine	85	(210)
Au	Gold	79	197·0
B	Boron	5	10·82
Ba	Barium	56	137·36
Be	Beryllium	4	9·013
Bi	Bismuth	83	209·00
Bk	Berkelium	97	(249)*
Br	Bromine	35	79·916
C	Carbon	6	12·011
Ca	Calcium	20	40·08
Cd	Cadmium	48	112·41
Ce	Cerium	58	140·13
Cf	Californium	98	(251)*
Cl	Chlorine	17	35·457
Cm	Curium	96	(247)
Co	Cobalt	27	58·94
Cr	Chromium	24	52·01
Cs	Caesium	55	132·91
Cu	Copper	29	63·54
Dy	Dysprosium	66	162·51
Er	Erbium	68	167·27
Es	Einsteinium	99	(254)
Eu	Europium	63	152·0
F	Fluorine	9	19·00
Fe	Iron	26	55·85
Fm	Fermium	100	(253)
Fr	Francium	87	(223)
Ga	Gallium	31	69·72
Gd	Gadolinium	64	157·26
Ge	Germanium	32	72·60
H	Hydrogen	1	1·0080
He	Helium	2	4·003
Hf	Hafnium	72	178·50
Hg	Mercury	80	200·61
Ho	Holmium	67	164·94
I	Iodine	53	126·91
In	Indium	49	114·82
Ir	Iridium	77	192·2
K	Potassium	19	39·100
Kr	Krypton	36	83·80
La	Lanthanum	57	138·92
Li	Lithium	3	6·940
Lu	Lutecium	71	174·99
Md	Mendeleevium	101	(256)
Mg	Magnesium	12	24·32
Mn	Manganese	25	54·94
Mo	Molybdenum	42	95·95
N	Nitrogen	7	14·008
Na	Sodium	11	22·991
Nb	Niobium	41	92·91
Nd	Neodymium	60	144·27
Ne	Neon	10	20·183
Ni	Nickel	28	58·71
Np	Neptunium	93	(237)
O	Oxygen	8	16
Os	Osmium	76	190·2
P	Phosphorus	15	30·975
Pa	Protoactinium	91	(231)
Pb	Lead	82	207·21
Pd	Palladium	46	106·4
Pm	Promethium	61	(147)*
Po	Polonium	84	(210)*
Pr	Praseodymium	59	140·92
Pt	Platinum	78	195·09
Pu	Plutonium	94	(242)
Ra	Radium	88	(226)
Rb	Rubidium	37	85·48
Re	Rhenium	75	186·22
Rh	Rhodium	45	102·91
Rn	Radon	86	(222)
Ru	Ruthenium	44	101·1
S	Sulphur	16	32·066 ±0·003
Sb	Antimony	51	121·76
Sc	Scandium	21	44·96
Se	Selenium	34	78·96
Si	Silicon	14	28·09
Sm	Samarium	62	150·35
Sn	Tin	50	118·70
Sr	Strontium	38	87·63
Ta	Tantalum	73	180·95
Tb	Terbium	65	158·93
Tc	Technetium	43	(99)*
Te	Tellurium	52	127·61
Th	Thorium	90	232·05
Ti	Titanium	22	47·90
Tl	Thallium	81	204·39
Tm	Thulium	69	168·94
U	Uranium	92	238·07
V	Vanadium	23	50·95
W	Tungsten	74	183·86
Xe	Xenon	54	131·30
Y	Yttrium	39	88·92
Yb	Ytterbium	70	173·04
Zn	Zinc	30	65·38
Zr	Zirconium	40	91·22

NOTES

1. This table is based on the 1957 report of the International Commission on Atomic Weights, as published in the 26 August, 1958 edition of the *Journal of the American Chemical Society*, volume 80.

2. The values given normally indicate the mean atomic weight of the mixture of isotopes found in nature. Particular attention is drawn to the value for sulphur, where the deviation shown is due to variation in relative concentration of isotopes.

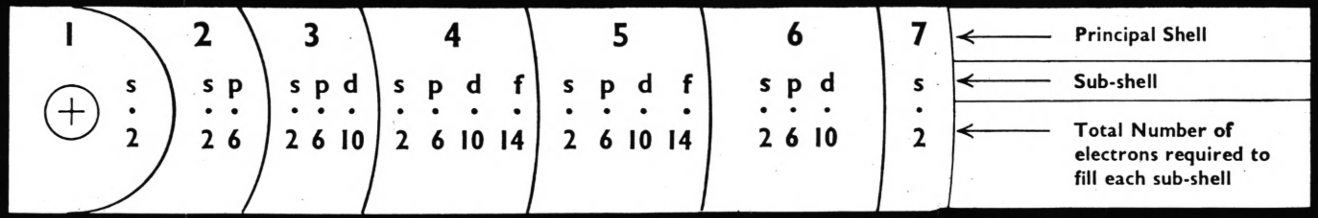
3. Bracketed values refer to the individual isotopes of radioactive elements. In most cases the value for the most long lived is given. Where, however, an asterisk occurs the atomic weight is that of the better known isotope.

PERIODIC TABLE OF THE ELEMENTS

1s	1 H	2 He
	s 1	s 2

	IA	IIA		IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB		IIIB	IVB	VB	VIB	VIIB	
2s	3 Li	4 Be												2p	5 B	6 C	7 N	8 O	9 F	10 Ne
3s	11 Na	12 Mg												3p	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4s	19 K	20 Ca	3d	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	4p	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5s	37 Rb	38 Sr	4d	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	5p	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6s	55 Cs	56 Ba	5d	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	6p	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7s	87 Fr	88 Ra	6d	89 Ac	d s 2 2	d s 3 2 4 1 3 2	d s 5 1 5 1 4 2	d s 5 2 6 1 5 2	d s 6 2 7 1 6 2	d s 7 2 8 1 7 2	d s 8 2 10 0 9 1	d s 10 1	d s 10 2		s p 2 1	s p 2 2	s p 2 3	s p 2 4	s p 2 5	s p 2 6
	s 1	s 2		d s 1 2																

4f	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	IIIA
4 f 5 s 5 p 5 d 6 s	2 2 6 0 2	3 —Outer sub-shells as for Ce—	4	5	6	7 f s p d s	7 2 6 1 2	9 2 6 0 2	10 —Outer sub-shells as for Ce & Tb—	11	12	13	14 f s p d s	14 2 6 1 2	
5f	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102	103	
5 f 6 s 6 p 6 d 7 s	0 2 6 2 2	2 2 6 1 2	3 —Outer sub-shells as for Pa—	4	5	6	7	8	9	10	11	12	13	14	



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