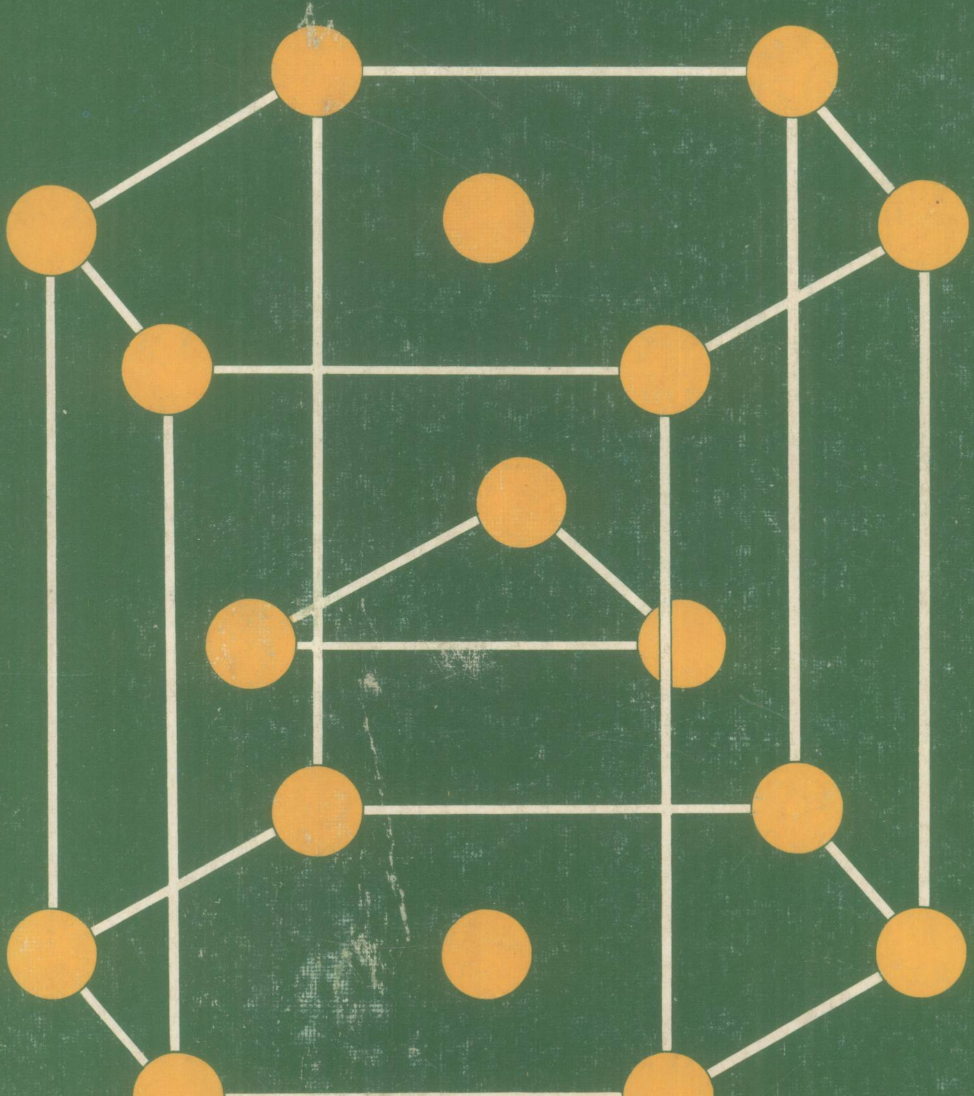
A Modern Approach to Comprehensive

CHEMISTRY

G.N. Gilmore



2nd Edition

06
G488-2
E2
8061995

A Modern Approach to Comprehensive Chemistry

Second Edition

G. N. Gilmore

Ph.D. C.Chem M.R.I.C.

Lecturer in Chemistry,
Bury College of Further Education

E8051995

Stanley Thornes (Publishers) Ltd

© 1979 G. N. Gilmore. This edition © 1979

All rights reserved. No part of this publication
may be reproduced, stored in a retrieval system, or
transmitted in any form or by any means, electronic,
mechanical, photocopying, recording or otherwise,
without the prior written consent of the copyright
holder.

First published 1975 by Stanley Thornes (Publishers) Ltd.,
EDUCA House, Liddington Estate, Leckhampton Road,
CHELTENHAM GL53 0D4
Reprinted with minor corrections 1977
Second Reprint 1978
Second Edition entirely reset 1979

ISBN 0 85950 015 2

The Publishers and the Author gratefully acknowledge the
permission of those bodies named to reproduce copyright
material used in this book as follows:

The University of London Entrance and School Examinations Council for permission to reproduce examination questions. The Joint Matriculation Board for authorising the reproduction of examination questions and for their permission to amend the wording in certain of these questions by the deletion of the words 'molecular weight' and the substitution of the words 'relative molecular weight'. Mr. J. E. White et al., compilers of TABLES FOR STATISTICIANS, 2nd Edition (Stanley Thornes (Publishers) Ltd., 1979) for permission to reproduce certain tables from that compilation. The Nuffield Foundation Science Teaching Project, and the Longman Group for their permission to reproduce selected physical properties from their PHYSICAL SCIENCES BOOK OF DATA; also for their permission to reproduce overhead projection original diagrams Nos. 4, 5, 6, 7, 8, 14, 19, 21, 23, 24 from the same source.

Typeset in 10/13 Times by
Malvern Typesetting Services Ltd, Malvern, Worcs.,
and printed and bound in Great Britain at
The Pitman Press, Bath

A Modern Approach
to Comprehensive
Chemistry

Chemistry

Also by Dr. G. N. Gilmore
A COMPLETE 'O' LEVEL CHEMISTRY
for 'O' Level J.M.B. and A.E.B. syllabuses

此为试读,需要完整PDF请访问: www.ertongbook.com

Preface to the First Edition

The object of this book is to present, in a concise manner, a comprehensive text to meet the requirements of the G.C.E. 'A' level chemistry syllabuses of the Joint Matriculation Board and the University of London. Obviously, it will also cover a large part of the syllabuses of similar examining bodies. The treatment is in line with current trends. Emphasis is therefore placed on general unifying principles rather than on a mass of unrelated facts.

The physical chemistry section opens with a consideration of atomic structure followed by states of matter, energetics, structure and bonding, equilibria, and kinetics. SI units are used along with those exceptions permitted by the above Examining Boards.

The physical and chemical properties of the elements and their compounds are largely determined by the electronic configuration of the constituent atoms. In the inorganic section, therefore, the book endeavours to show how the relationship arises and how it is applied in correlating the chemistry of the elements.

The organic section is treated as the chemistry of the functional groups and mechanisms are given wherever practicable. The book is not intended to present an exhaustive account of preparations and properties.

Nomenclature throughout is that recommended by the 1972 report of the Association for Science Education. However, the oxidation number of the elements has been omitted if it is the only one normally encountered. In the case of oxoacids, the oxygen content has been included (e.g. tetraoxosulphuric(VI) acid) but these names may be abbreviated if desired. Trivial names are given (in brackets) in order to aid the transition to systematic naming. For convenience, both systematic and trivial names are given in the index.

Physical data in the text has been extracted, wherever possible, from the Nuffield Book of Data and I am grateful to the Nuffield Foundation for permission to do this. I am further indebted to the same body for permission to reproduce 11 of their diagrams on periodicity. I also wish to thank the Joint Matriculation Board (J.M.B.) and the University of London for permission to use questions from their Advanced level examinations and to include in these I.U.P.A.C. nomenclature where necessary.

G.N.G.

Preface to the Second Edition

The basic structure of the first edition has been maintained. However, a number of minor modifications have been made as well as including, wherever possible, the states of substances in equations. Additional material includes the van der Waals equation, liquefaction of gases, radius ratios, calculation of the Avogadro constant from unit cell measurements, dipole moments, steam distillation calculations, and methods for deriving half-reactions for oxidations and reductions. The section on mass spectroscopy has been extended and its use in structure determination of organic molecules has been indicated. An extra chapter on selected reactions of some cations and anions has been included. Finally, for the sake of simplicity, the oxygen content of oxoacids and their salts has been omitted.

In conclusion, I would like to take this opportunity of thanking all those who have written in support of the book and for a number of helpful suggestions they have made.

G.N.G.

8061995

Contents

华南工学院
外国教材
中心图书室藏书

8061995

1 Atomic Structure

东南工学院
中心图书[illegible]

ATOMS, MOLECULES, AND IONS

Atoms are the smallest particles of elements that can take part in chemical changes. It is known that they consist of a number of fundamental particles, the most important of which are *electrons, neutrons,* and *protons*. The neutrons and protons make up the nucleus and this is surrounded some distance away by the electrons. The properties of these particles are summarised in Table 1.1.

Table 1.1. Properties of the fundamental particles

Name of Particle		*Mass*	*Charge*
Proton	Sometimes referred to as nucleons	1 unit	Positive
Neutron		1 unit	Neutral
Electron		Negligible compared with neutrons and protons, i.e. 1/1836 unit	Negative

Since all atoms are electrically neutral, they must contain the same number of electrons and protons. There is, however, no simple relationship between the number of protons and neutrons in an atom.

In between the nucleus and electrons is space, in fact the bulk of the volume of an atom is space, the radius of the nucleus being about 1/10 000 of the radius of the atom as a whole.

The number of protons in the nucleus is known as the *atomic number, Z*, of the element. The atomic number is important since it determines the identity of the element and also its properties.

A number of elements have atoms which are not stable under normal conditions and, in many of these cases, the atoms link up to form *molecules* which are stable. A molecule is the smallest particle of a substance that can exist by itself. Atoms of sodium, magnesium, iron, helium, etc. are stable and so atoms and molecules of these elements are the same; the molecules are said to be *monatomic*. Molecules of oxygen, chlorine, nitrogen, etc. contain two atoms and are said to be *diatomic*. Higher atomicities also occur, for example, P_4 and S_8.

Ions are produced when atoms lose or gain electrons, for example

$$\begin{array}{ll} \mathrm{Na} - e^- \rightarrow \mathrm{Na}^+, & \mathrm{Mg} - 2e^- \rightarrow \mathrm{Mg}^{2+} \\ \mathrm{Cl} + e^- \rightarrow \mathrm{Cl}^-, & \mathrm{S} + 2e^- \rightarrow \mathrm{S}^{2-} \end{array}$$

Isotopes

Isotopes are atoms of the same element that differ only in their mass; that is, they have different numbers of neutrons in their nuclei. For example, there are two naturally occurring isotopes of chlorine: chlorine atoms containing 17 protons, 17 electrons, and 18 neutrons and chlorine atoms with 17 protons, 17 electrons, and 20 neutrons. These two isotopes are represented as $^{35}_{17}Cl$ and $^{37}_{17}Cl$ respectively, the subscript being the atomic number, Z, and the superscript the *mass number*, A, which is the mass of the isotope to the nearest whole number.

In general, it is found that elements with even atomic numbers have many more isotopes than those with odd numbers. In fact, if the atomic number is odd, it is rare to find an element with more than two stable isotopes.

It quite often happens that isotopes of different elements have the same mass numbers and such isotopes are termed *isobars*; $^{40}_{18}Ar$, $^{40}_{19}K$, and $^{40}_{20}Ca$ are a set of isobars.

Relative atomic mass, A_r

The mass of a hydrogen atom is 1.673×10^{-27} kg and, although some elements have atoms over two hundred times as heavy as this, the figures involved are far too small to have any general practical use. For this reason, the masses of atoms relative to one particular atom are determined, the standard being the $^{12}_{6}C$ isotope. *Relative atomic mass* may be defined as the number of times an atom of the element is heavier than 1/12 of the mass of the $^{12}_{6}C$ isotope. Most of the values so obtained are not integers because elements obtained from natural sources consist of mixtures of their isotopes. A further reason is that the electrons have a small mass, and neutrons and protons do not have precisely the same mass (see under radioactivity).

EVIDENCE FOR SUB-ATOMIC PARTICLES

a. Electrons

The discovery of electrons was due to J. J. Thomson at the end of the nineteenth century. He found that, if an electric discharge is passed through a gas at low pressure (10^{-6} atmospheres), a beam of rays is emitted perpendicularly from the cathode. These rays can be deflected by applying a magnetic field across their path (Figure 1.1); this indicates that the rays are charged.

If an electric field is applied to them, the rays are deflected towards the positive pole indicating that they are negatively charged. Thomson was able to determine the ratio of charge to mass, e/m, of the rays by measuring the angles through which they were deflected by known magnetic and electric fields. This ratio was found to be constant regardless of the gas used and so the uniformity of the particles, i.e. electrons, was apparent.

The charge on an electron was determined a few years later by Millikan using an apparatus similar to that in Figure 1.2.

The method involves letting very small drops of oil fall between the two metal

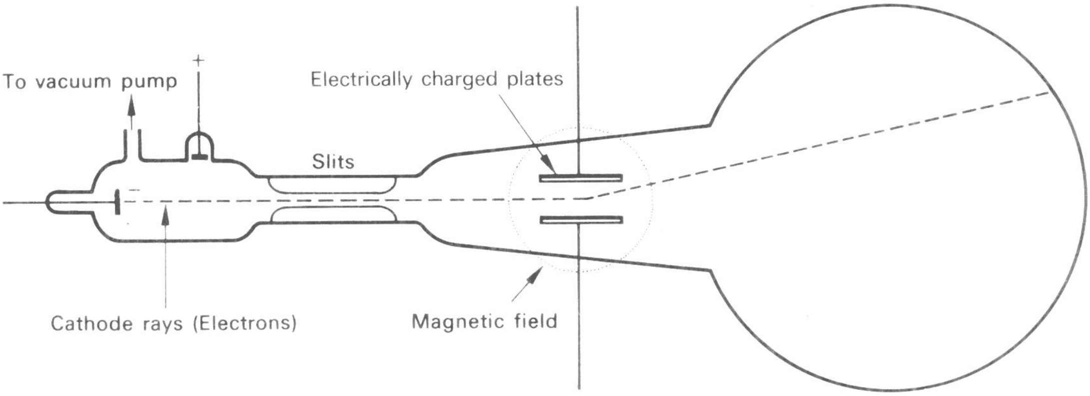


Figure 1.1 Deflection of cathode rays (electrons) by electric and magnetic fields

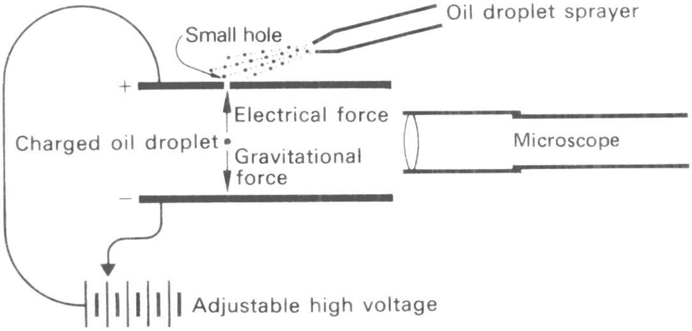


Figure 1.2 Apparatus for the Millikan oil drop experiment

plates by means of the small hole. Electrons are then produced by passing a beam of X-rays through the air above the upper plate and some of them are accepted by the drops so giving them a negative charge. The rate of fall of a drop is determined by observing it through a microscope fitted with a transparent scale, and from this the mass of the drop can be calculated. The upper and lower plates are then connected to the positive and negative terminals respectively of an adjustable high-voltage source. By adjusting the strength of the electrical field, it is possible to balance the gravitational force on the negatively charged drop against the electrical force tending to make it rise, and so the drop remains stationary.

The electrical force on the drop can be calculated in terms of its charge and the electrical field between the plates. When the charged drop is held stationary, the electrical force equals the mass of the drop and so the charge on the drop can be calculated.

No matter how many times the experiment is repeated, it is always found that the charge on the drop is some integer times 1.602×10^{-19} coulomb. Since the smallest charge Millikan found on a drop was 1.602×10^{-19} coulomb, this was taken to be the charge on a single electron.

Once Millikan had determined the charge and Thomson the charge/mass ratio, it was possible to calculate the mass of an electron. The electron mass is 9.109×10^{-31} kg.

此为试读，需要完整PDF请访问：www.ertongbook.com

b. Protons

As well as giving a stream of electrons from the cathode, the passage of an electric discharge through a gas at low pressure also gives a stream of positive rays from the anode. The charge on these particles is illustrated by their behaviour in magnetic and electric fields. The mass of these positive ions can be determined very accurately by means of a mass spectrograph, the basis of which is shown in Figure 1.3.

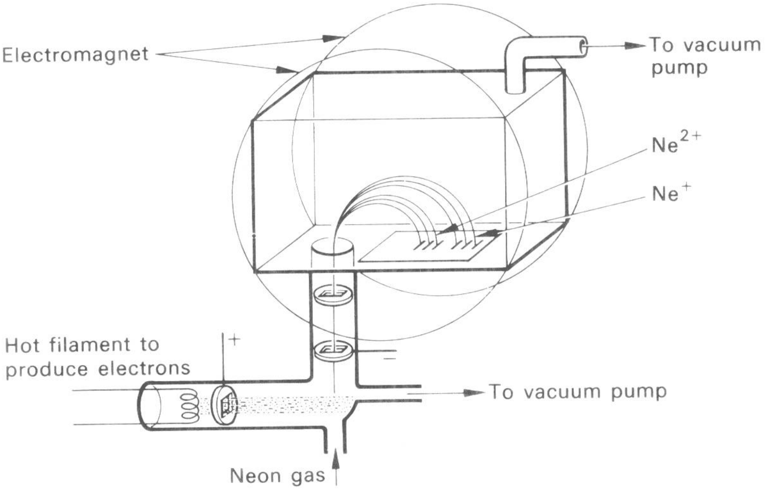


Figure 1.3 A mass spectograph

The beam of electrons from the filament collides with some of the neon atoms (or atoms of any other gas or vapour being tested) and dislodges electrons from them so producing positive ions.

These ions, for example, Ne^{+} and Ne^{2+}, are accelerated to the negative electrode by its high charge. The beam emerging through the slit in the negative electrode passes through another slit into a chamber which is situated between the poles of a powerful electromagnet. This causes the positive ions to move in a circular path, those with high charges moving along an arc of small radius whilst those with high masses move along an arc of large radius. Each positive ion therefore has its own characteristic path determined by its charge and mass. The positive ions then impinge on a photographic plate which, after development, shows a series of lines. The mass of an ion can then be calculated from a knowledge of the electron charge, the radius of the circular path followed, the number of charges on the ion, the strength of the magnetic field, and the voltage between the positive and negative electrodes (this determines the velocity of the ion).

The mass spectrograph for neon, as shown in Figure 1.3, gives a series of three lines for Ne^{+} and for Ne^{2+} ions. This indicates that neon is a mixture of three isotopes, i.e. neon has atoms having three different masses depending upon the number of neutrons present.

Mass spectrographs have been replaced by mass spectrometers, the essentials of which are shown in Figure 1.4. The sample, if not gaseous, is vaporised and then it passes at very low pressure into the main chamber. The vapour is bombarded

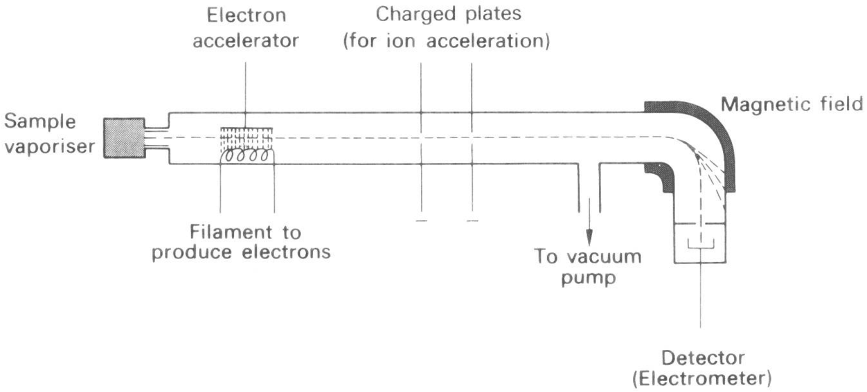


Figure 1.4 Mass spectrometer

with high-energy electrons and some collisions will result in electron loss from the sample with the formation of positive ions. The ions are then accelerated by passage through slits in two plates to which an electric field is applied. At this stage, the positive ions have similar velocities but different charge/mass ratios. They now pass through a magnetic field and are deflected by it, the deflection produced by a given magnetic field depending on the charge/mass ratio of the ion. The magnetic field is gradually adjusted so that ions with different charge/mass ratios are focused, in turn, on the detector. The detector consists of a conductor connected to an electrometer. The relative abundance of each type of ion affects the charge on the electrometer. The mass of an ion and its relative abundance are indicated by a peak on a chart.

Although passing an electric discharge through different gases at low pressure always gives identical negatively charged rays, the positively charged rays are different. The value of *e*/*m* for these rays is much smaller than the value for electrons but the largest value is obtained when hydrogen is the source material. Hence it is assumed that the hydrogen nucleus contains a single positive particle, the proton.

c. Neutrons

The existence of neutrons was suggested as a result of experiments done by Rutherford, Geiger, and Marsden using the apparatus shown schematically in Figure 1.5.

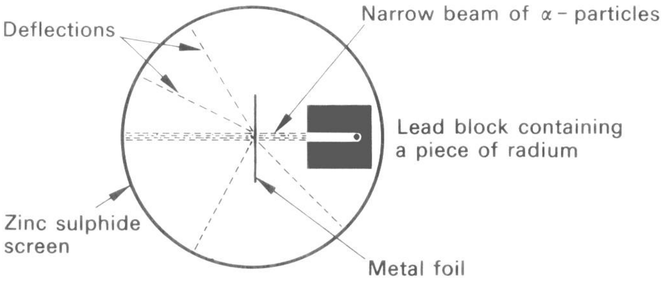


Figure 1.5 Apparatus used in the discovery of neutrons

A piece of radium is placed in a small hole in a lead block to give a narrow beam of α-particles (page 7) and this beam is directed at a very thin piece of gold foil (about 10 000 atoms thick). The foil and lead block are situated in an evacuated vessel with a zinc sulphide screen which emits a flash of light every time an α-particle strikes it, the flashes being detected and counted with the aid of a microscope. It is found that most of the α-particles pass straight through the foil with little or no deviation but a few are deflected, sometimes through angles which approach 180°.

At the time, atoms were thought by Thomson to be uniform-density balls containing electrons embedded in the protons and, from the physical properties, it was inferred that in solids the atoms were close together. If this were the case, however, an α-particle with sufficient kinetic energy to force its way through 10 000 atoms would undergo little or no deflection. The fact that some large deflections occurred refuted Thomson's concept. Rutherford suggested that atoms, in fact, occupy a spherical volume with a radius of about 10^{-10} m, the electrons moving round a central positively charged nucleus, which contains most of the mass of the atom, and which has a radius of about 10^{-14} m. An atom on this hypothesis is therefore mostly space. Hence α-particles will readily push past the electrons and will be deflected to an appreciable extent only when they approach the nucleus of an atom. Not only are most nuclei bigger than α-particles but they are also positively charged and so they exert a considerable repulsive force on them when they come close together; large deflections are therefore possible.

Rutherford found that he could determine the charge on the nucleus from the pattern made by the deflected α-particles, since the greater the charge on the nucleus, the greater the deflections. This proved to be an accurate method after various improvements had been made to the apparatus. Rutherford then observed that there was no correlation between the actual mass of an atom (as determined by chemical means or by the mass spectrograph) and the total mass of the protons and electrons present and so he suggested the existence of a neutral particle in the nucleus.

In 1930, Bothe and Becker discovered a new type of 'radiation' by irradiating beryllium with α-particles. Two years later Chadwick analysed this 'new radiation' and found that its properties were consistent with it being neutral particles, i.e. neutrons.

RADIOACTIVITY

In 1896, Becquerel found that uranium salts could discharge an electroscope and affect a photographic plate. Two years later Mme Curie and Schmidt found that thorium compounds behaved similarly. Compounds such as this are said to be *radioactive.*

Many naturally occurring radioactive substances are now known. All isotopes with atomic number greater than 83 are radioactive but many radioactive isotopes of the lighter elements can be made artificially by bombarding various elements with α-particles, neutrons, protons, or deuterons (^2_1H), etc.

There are three methods of detecting radioactivity.

(a) The action on a photographic plate.

(b) The fluorescence produced in some compounds, e.g. zinc silicate, zinc sulphide, etc.

(c) By its ionisation of gases.

The last method is the most important, the presence of ionised gases being demonstrated by the fact that they discharge a charged gold leaf electroscope.

By nearly surrounding a piece of radium with sheets of metal foil and using strong magnetic or electric fields and an electroscope, it is possible to show that the radium emits three types of rays (Figure 1.6).

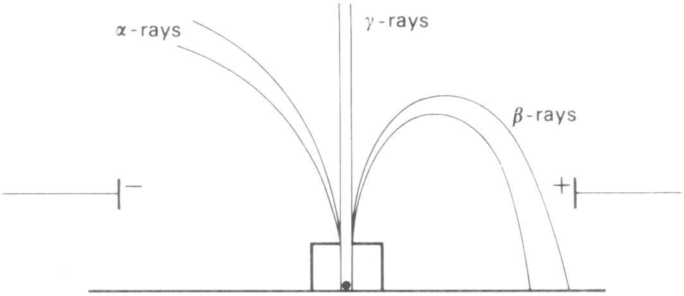


Figure 1.6 Behaviour of α-, β-, and γ-rays in magnetic and electric fields

(i) α-Rays

These are fast moving positively charged particles having a mass of four and two units of positive charge, i.e. helium nuclei. They have a powerful ionising effect on any gases they pass through but they are readily absorbed by, for example, about 7cm of air or a sheet of paper. The actual path of an α-particle can be seen by the Wilson cloud chamber method in which an α-particle is allowed to pass through a gas supersaturated with water vapour. The α-particle ionises the gas and the ions act as centres for condensing the water vapour so that a vapour trail can be seen. The path of an α-particle is affected by a magnetic field.

(ii) β-Rays

These are fast moving electrons with velocities near to that of light. They have considerably more penetrating power than α-particles but are much less effective at ionising gases due to their smaller mass and kinetic energy. The path of β-rays is greatly affected by a magnetic field.

(iii) γ-Rays

These are electromagnetic radiations with the speed of light and identical with very short wavelength X-rays. They are very penetrating and will, for example, penetrate several cm of lead, etc. Their path is unaffected by magnetic fields. They are emitted in conjunction with α- or β-rays and are merely a means of getting rid of excess energy from a nucleus formed in an excited state. Since γ-rays are uncharged, they do not readily cause ionisation on passing through matter.

Reasons for radioactivity

Rutherford and Soddy (1903) suggested that the nuclei of radioactive elements are unstable and that spontaneous disintegrations take place to give the nuclei of different elements. The reason for the instability becomes apparent when the actual masses of isotopes, relative to ${}^{12}_{6}C$, are compared with the expected masses from the constituent particles. The expected masses may be calculated given that the masses of protons, neutrons, and electrons are 1.007276, 1.008665, and 0.000549 atomic mass units respectively.

Example Comparison of the actual and calculated masses of the radioactive ${}^{13}_{8}O$ and the stable ${}^{16}_{8}O$ isotopes:

Expected mass of ${}^{13}_{8}O = (8 \times 1.007276) + (8 \times 0.000549) + (5 \times 1.008665) = 13.105925$ a.m.u.
Actual mass as shown by mass spectroscopy = 13.024799 a.m.u.
Difference, i.e. expected mass − actual mass = 0.081126 a.m.u.
Expected mass of ${}^{16}_{8}O = (8 \times 1.007276) + (8 \times 0.000549) + (8 \times 1.008665) = 16.131920$ a.m.u.
Actual mass as shown by mass spectroscopy = 15.994915 a.m.u.
Difference = 0.137005 a.m.u.

It is seen that there is a net loss in mass on forming the isotopes from their constituent particles. This loss in mass is known as the *mass defect* and corresponds to the energy that would be required to split the atom into its constituent particles (energy is related to mass according to Einstein's equation $E = mc^2$—see page 14). The energy which appears to have been released in the formation of the atom is known as the *binding energy*. From the example above it is evident that stable isotopes have larger mass defects and binding energies than radioactive ones.

Consequences of radioactive decay

If an atom emits an α-particle, the resultant atom will have an atomic number of two less than the original and a relative atomic mass of four less. On the other hand, if an atom emits a β-particle, the resultant atom will have an atomic number one higher but the same relative atomic mass because, in the process, a neutron disintegrates to give an electron and a proton:

$$ {}^{1}_{0}n \rightarrow {}^{1}_{1}p + {}^{\;0}_{-1}e $$

It often happens that the isotope of the new element formed is radioactive and so the radioactive decay continues until a stable nucleus is formed. For example, uranium, thorium, and actinium all disintegrate to give isotopes of lead as the final product.

A plot of neutrons against protons for the stable isotopes of the various elements gives a graph of the form shown in Figure 1.7. Any isotopes not lying in the stability region are radioactive and undergo decay until an atom is formed which is in the stable band. It is seen that, up to about atomic number twenty, the stable atoms have a proton : neutron ratio of 1 : 1 but, above this point, the neutrons predominate. There is no definite way of predicting how a radioactive atom will decay but some generalisations may be made. Naturally occurring

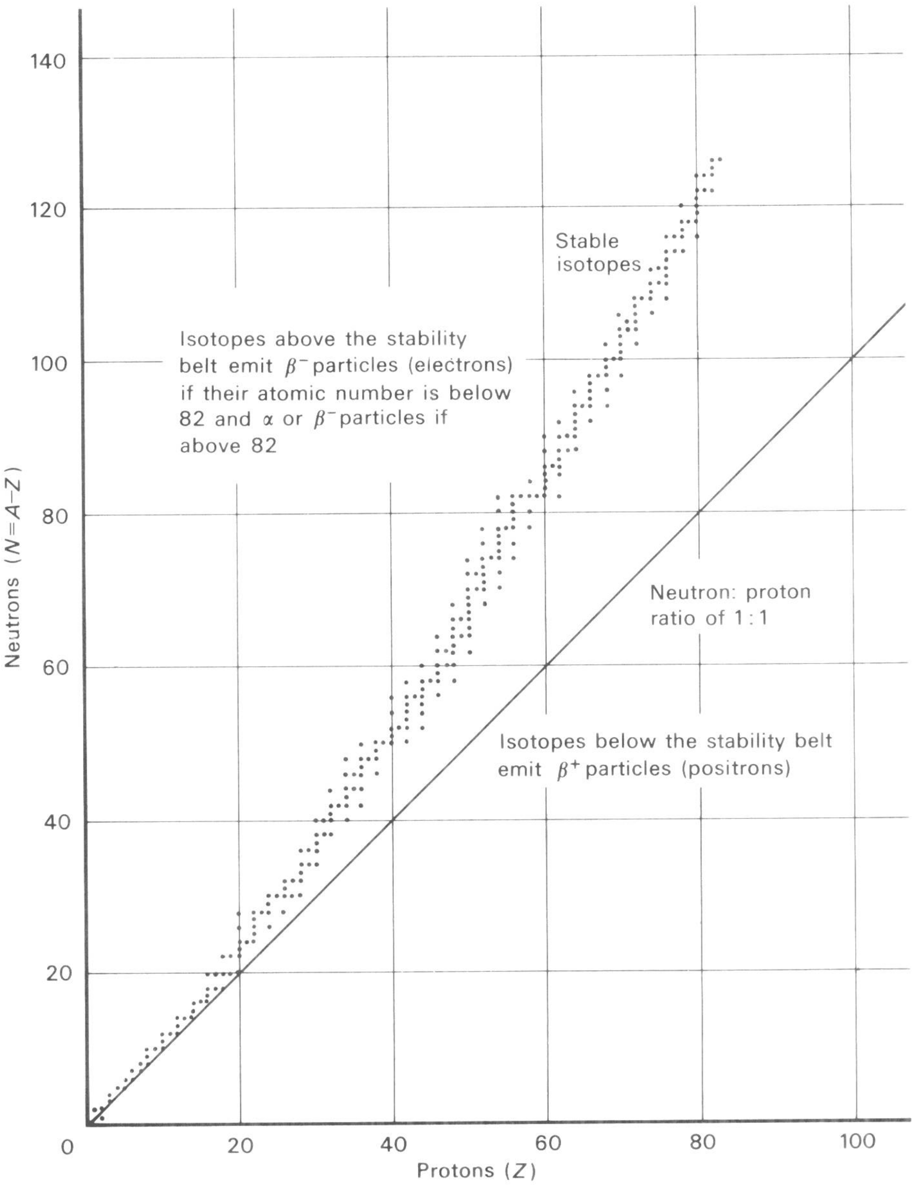


Figure 1.7 Plot of neutrons against protons for stable isotopes

isotopes with atomic number less than 82 do not show α-activity but emit β-particles if they have more neutrons than the stability band. Above atomic number 82, α- and/or β-activity is possible. An element having fewer neutrons than the stable isotopes of that element will rectify this by undergoing *positron* (a positively charged electron, e^+) emission:

$$^{1}_{1}\mathrm{p} \rightarrow {}^{1}_{0}\mathrm{n} + {}^{0}_{1}\mathrm{e}$$

Half-lives of radioactive isotopes

The rate of decay of a radioactive isotope is characteristic of the isotope and is usually expressed in terms of its *half-life*, $t_{\frac{1}{2}}$. The half-life is the time taken for

此为试读，需要完整PDF请访问：www.ertongbook.com