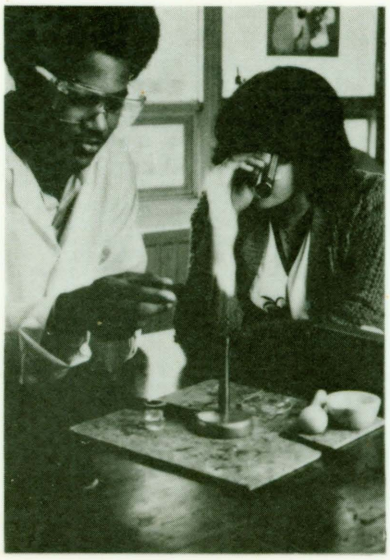
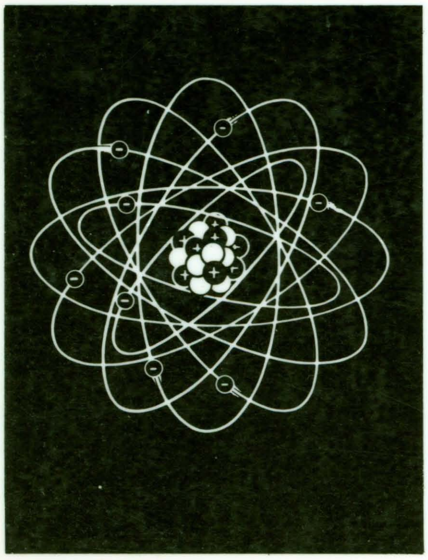
ILPAC

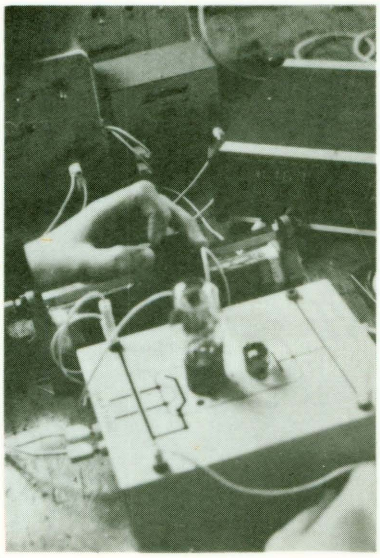
UNIT S2

INDEPENDENT LEARNING PROJECT FOR ADVANCED CHEMISTRY

Atomic Structure







Periodic Table of the Elements

I	II											III	IV	V	VI	VII	O
						1 H 1.0											2 He 4.0
3 Li 6.9	4 Be 9.0											5 B 10.8	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc 99.0	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 210.0	85 At 210.0	86 Rn 222.0
87 Fr 223.0	88 Ra 226.0	89 Ac 227.0															

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.1	93 Np (237)	94 Pu 239.1	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lw (257)

A value in brackets denotes the
mass number of the most stable isotope.

UNIT

S2

Atomic Structure

First published 1983
by John Murray (Publishers) Ltd
50 Albemarle Street
London W1X 4BD

Reprinted 1984, 1985

Printed and bound in Great Britain by
Martin's of Berwick

British Library Cataloguing in Publication Data

Independent Learning Project for Advanced
Chemistry
Atomic Structure. - (ILPAC; Unit S2)
1. Science
I. Title II. Series
500 Q161.2

ISBN 0 7195 4036 4

CONTENTS

APPENDIX ONE

APPENDIX TWO

APPENDIX THREE

PREFACE

This volume is one of twenty Units produced by ILPAC, the Independent Learning Project for Advanced Chemistry, written for students preparing for the Advanced Level examinations of the G.C.E. The Project has been sponsored by the Inner London Education Authority and the materials have been extensively tested in London schools and colleges. In its present revised form, however, it is intended for a wider audience; the syllabuses of all the major Examination Boards have been taken into account and questions set by these boards have been included.

Although ILPAC was initially conceived as a way of overcoming some of the difficulties presented by uneconomically small sixth forms, it has frequently been adopted because its approach to learning has certain advantages over more traditional teaching methods. Students assume a greater responsibility for their own learning and can work, to some extent, at their own pace, while teachers can devote more time to guiding individual students and to managing resources.

By providing personal guidance, and detailed solutions to the many exercises, supported by the optional use of video-cassettes, the Project allows students to study A-level chemistry with less teacher-contact time than a conventional course demands. The extent to which this is possible must be determined locally; potentially hazardous practical work must, of course, be supervised. Nevertheless, flexibility in time-tabling makes ILPAC an attractive proposition in situations where classes are small or suitably-qualified teachers are scarce.

In addition, ILPAC can provide at least a partial solution to other problems. Students with only limited access to laboratories, for example, those studying at evening classes, can concentrate upon ILPAC practical work in the laboratory, in the confidence that related theory can be systematically studied elsewhere. Teachers of A-level chemistry who are inexperienced, or whose main discipline is another science, will find ILPAC very supportive. The materials can be used effectively where upper and lower sixth form classes are timetabled together. ILPAC can provide 'remedial' material for students in higher education. Schools operating sixth form consortia can benefit from the cohesion that ILPAC can provide in a fragmented situation. The project can be adapted for use in parts of the world where there is a severe shortage of qualified chemistry teachers. And so on.

A more detailed introduction to ILPAC, with specific advice both to students and to teachers, is included in the first volume only. Details of the Project Team and Trial Schools appear inside the back cover.

LONDON 1983

ACKNOWLEDGEMENTS

Thanks are due to the following examination boards for permission to reproduce questions from past A-level papers.

Joint Matriculation Board:

Teacher-marked Exercise, p70(1977)

Oxford Delegacy of Local Examinations

Exercise 74 (1980)
End-of-Unit Test 11(1979)
Teacher-marked Exercise, p82(1979 & 1980)

University of Cambridge Local Examinations Syndicate

Exercise 13 (1977)
Level One Test 13(1975)
End-of-Unit Test 12(1974)

University of London Entrance and School Examinations Council

Exercises 7(1976), 72(1973)
Level One Test 1(N 1977), 2(N 1980), 3(L 1977), 4(L 1982), 5(L 1978) 6(L 1979)
7(L 1979), 8(L 1975), 9(N 1975), 10(N 1978),
11(L 1980), 12(L 1981)
End-of-Unit Test 1(L 1982), 2(L 1982), 3(L 1982), 4(N 1976), 5(N 1975),
6(L 1978), 7(N 1978), 8(L 1976), 9(N 1975), 10(L 1979),
13(L 1973), 14(L 1981), 16(N 1979)

Welsh Joint Education Committee

Exercises 71(1979), 73(1978)

Questions from papers of other examining boards appear in other Units.

Where answers to these questions are included, they are provided by ILPAC and not by the examination boards.

Photographs are included by permission as follows:

Fig. 8: Albert Einstein - Camera Press Ltd.

Fig. 13: Mushroom cloud and Hiroshima 1945 - Popperfoto

Photographs of students and Fig. 14: Mobaltron Cobalt Unit - Tony Langham

Fig. 25: X-ray and electron diffraction photographs - Alan Mackay, Birkbeck College

SYMBOLS USED IN ILPAC UNITS

Reading

Exercise

Test

A 'A' Level question

A part 'A' Level part question

sA 'A' Level question
Special paper

W Worked example

✓ Teacher-marked exercise

Revealing exercises

Discussion

C Computer programme

Experiment

Video programme

Film loop

Model-making

INTERNATIONAL HAZARD SYMBOLS

✖ Harmful

Flammable

Corrosive

☠ Toxic

Explosive

Oxidising

☢ Radioactive

INTRODUCTION

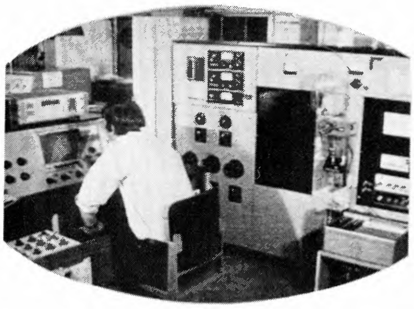
Elements differ from one another because they have different atoms. Every atom consists of a central nucleus surrounded by electrons.

In Level One we describe the composition of the nucleus. The nucleus can be regarded as a grouping of even smaller particles: protons and neutrons. For a given element, all atoms have the same number of protons in the nucleus, but different isotopes of the element contain different numbers of neutrons. We show how an instrument called the mass spectrometer gives us a lot of information about nuclei. We also describe how nuclei decompose (radioactivity) and other aspects of nuclear chemistry.

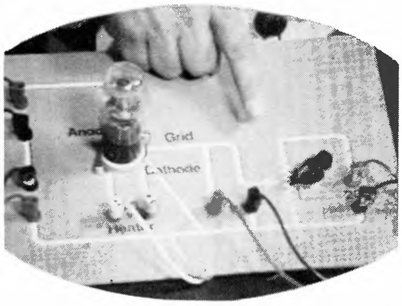
The total number of extra-nuclear electrons (i.e. electrons surrounding the nucleus) also varies from element to element. In Level Two, we describe how these electrons are arranged in different shells, and how a shell may have several sub-shells consisting of one or more orbitals. We present evidence for the way in which electrons are arranged outside the nucleus, by considering firstly ionization energies and secondly, emission spectra.

There are two experiments in the Unit - the electron impact method for determining ionization energy and a qualitative examination of spectra of some *s*-block elements using a hand spectroscope.

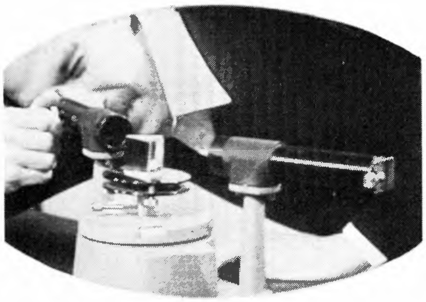
There are three video-programmes designed to accompany this Unit. Their use is not essential, but you should try to see them at the appropriate time if they are available.



Instrumental techniques



Ionization energy



The hydrogen spectrum

PRE-KNOWLEDGE

Before you start work on this Unit you should be able to:

(1) explain each of the following terms:
  (a) element
  (b) atom
  (c) ion
  (d) relative atomic mass
  (e) mole
  (f) the Avogadro constant, L
  (g) frequency
  (h) wavelength

(2) state the relative masses and charges of the three fundamental particles in the atom;

(3) describe, at a simple level, a planetary model of the atom, using the terms: proton, neutron, electron, nucleus, shell (or orbit);

(4) write down the names, symbols and atomic numbers of the first twenty elements in the Periodic Table;

(5) write out the electron arrangements of the first twenty elements in the Periodic Table, using the style: Na - 2.8.1.;

(6) write equations for the formation of ions from atoms.

PRE-TEST

To find out whether you are ready to start Level One, try the following test, which is based on the pre-knowledge items. You should not spend more than 30 minutes on this test. Hand your answers to your teacher for marking.

PRE-TEST

1. Copy and complete the following table to summarise the properties of the three fundamental particles found in an atom.

Table 1

Fundamental particle	Relative mass	Relative charge
proton		
neutron		
electron		

(6)

2. Identify the numbered elements in the following extract of the Periodic Table

Li	Be	B	(1)	N	O	F	(2)
(3)	Mg	Al	Si	P	(4)	Cl	Ar
K	(5)						

Fig. 1.

(5)

3. The electron configuration of magnesium is represented by 2.8.2. Write the corresponding configurations for:

(a) lithium,

(b) nitrogen,

(c) silicon. (3)

4. The way in which potassium normally ionises is represented by:

$$K \rightarrow K^+ + e^-$$

Write similar equations for the ionisation of:

(a) magnesium,

(b) chlorine,

(c) oxygen. (6)

5. Explain why neon does not ionise in normal chemical reactions. (1)

6. Which of the following statements about an atom is not true?

The atomic number Z represents:

A the number of electrons going round the nucleus,

B the positive charge on the nucleus,

C the number of neutrons in the nucleus,

D the element's position in the Periodic Table. (1)

7. Fig. 2 represents a generalised form of radiation:

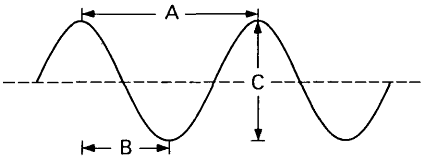


Fig. 2.

Which letter represents the wavelength of the radiation? (1)

8. Radiation is often identified by its frequency. Which of the following are units of frequency?

A cm s^{-1}

B m s^{-2}

C s^{-1}

D m s^{-1}

E min^{-1} (2)

(Total 25 marks)

LEVEL ONE: THE NUCLEUS

We start this Unit by considering the size of an average atom and the relative size of its nucleus.

Objective. When you have finished this section, you should be able to:

(1) calculate the density of an atomic nucleus, given the nuclear volume, V_N.

RELATIVE SIZES

Atomic size obviously varies from element to element. Radii lie within the range 0.05 - 0.20 nm.* The following exercise helps you appreciate how small this is.

*1 nanometre, nm = 10^{-9} m (nano comes from the Greek word meaning dwarf).

Exercise 1 Suppose a football, diameter 22 cm, is scaled up so that it becomes as big as the earth, diameter 13000 km. Calculate whether an atom of diameter 0.32 nm will become as big as:

A a pin-head, diameter 1 mm,

B a 1p piece, diameter 1.9 cm,

C a football, diameter 22 cm,

D a weather balloon, diameter 1.8 m.

(Answer on page 85)

How big is the nucleus?

An atom is small, but its nucleus is smaller still. While the radius of an atom is of the order of 10^{-10} m, that of a nucleus is of the order of 10^{-15}m. Do the next exercise to help you appreciate the difference in size.

Exercise 2 If the nucleus of an atom were scaled up to the size of a pin-head (say 1 mm diameter), how big would the atom be?

(Answer on page 85)

Since the mass of an atom is concentrated in its nucleus, the nucleus must be extremely dense. Estimate how dense it is by doing the next exercise.

Exercise 3 For atoms of elements at the beginning of the Periodic Table the nuclear volume, V_N, is given by:

$$V_N = 1.73 \times (\text{relative atomic mass}) \times 10^{-45}\ \text{m}^3$$

Use this expression to calculate the density of the sodium nucleus:

(a) in kg m^{-3}

(b) in ton mm^{-3}

(Answers on page 85)

Were you surprised by the magnitude of this number? The next exercise will help you appreciate how much empty space there is in an atom.

Exercise 4 Calculate:

(a) the volume occupied by a sodium atom (radius 0.186 nm),

(b) the fraction of the volume occupied by the nucleus.

Hint: assume that both the atom and its nucleus are spherical. The volume of a sphere is given by: $\frac{4}{3}\pi r^3$ where r is the radius of the sphere.

(Answers on page 85)

Most of your body is empty space too. If all the spaces between the nuclei were squeezed out, you would be only half as big as a flea, although your weight would be the same.

In view of this, you may be wondering why any object appears solid. The electrons in an atom move very rapidly around the nucleus, somewhere within a particular radius. The electrons effectively form a shield around the nucleus, marking the limits of the atom's volume and making it seem solid.

You now go on to revise atomic number and mass number and find out more about isotopes.

ATOMIC NUMBER, MASS NUMBER AND ISOTOPES

Atomic number and mass number give us important information about an atom and are particularly useful in distinguishing one isotope of an element from another.

Objectives. When you have finished this section you should be able to:

(2) define the terms atomic number, Z and mass number, A;

(3) explain what isotopes are;

(4) use values for atomic number and mass number to calculate the number of protons and neutrons in the nucleus;

(5) use isotopic symbols to describe the composition of a nucleus, e.g. $^{12}_{6}C$.

You will have noticed that certain words or phrases in the objectives are emphasised - we call these keywords. Keywords help you to use the index of a book to find the relevant sections to read, and may also help you to organise your notes.

The next task for you to do is some reading. We always identify reading tasks by a symbol in the margin - see below. Since this is the first reading task you have met in the course so far, we give some notes of guidance which you should study before carrying out the task.

Read about atomic number and mass number in your text-book(s), and find out what isotopes are.

Guidance for reading

1. *Give yourself enough room to work - somewhere you can spread out your books and paper.*

2. *Go through the objectives listed before the reading task, noting the keywords. There may also be some extra keywords in the reading task itself. (In this particular task, the keywords in Objectives 2 and 3 are the ones to focus on.) Look up the keywords in the index of your text-book(s) and note the page numbers.*

3. *Turn to the page references for each objective and scan* each page in turn, looking out for the keywords. In this way, identify sections that contain relevant information.*

4. *Skim* each of the sections you've identified, bearing in mind what you want to find out. You know this from the objectives and also by looking at the exercises which come directly after the reading.*

5. *Read the passage(s) intensively*.*

6. *Do the exercise(s) which follow the reading. These are designed to test your understanding of what you've just read, so you may find that you need to re-read the passage.*

7. *Having done the exercise(s), look back at the objectives. Do they include anything not covered by the exercises? If so, make a note of the missing items, under the section heading.*

** 'scanning', 'skimming' and 'intensively reading' were explained in "Introduction to ILPAC: for the Student", (Unit S1: The Mole, p.vii). Look back at this if you aren't sure what we mean by these terms.*

You should now be able to answer Exercises 5 and 6.

Exercise 5 Define the terms atomic number and mass number.

(Answers on page 85)

Exercise 6 Explain what isotopes are and give an example, using nitrogen.

(Answer on page 85)

Now that you have revised these terms, go on to the next exercise, which is part of an A-level structured question.

At appropriate points throughout the course we include questions similar to those you might encounter in an A-level examination. These questions are identified by symbols in the margin (the letter 'S' denotes Special paper standard).

A S A A part

Where these questions are taken from past examination paper, the examining board and the year are identified in the acknowledgements section at the beginning of the Unit.

Exercise 7 The table shows the mass number and number of neutrons in the nucleus, for four atoms, W, X, Y and Z.

A part

	W	X	Y	Z
Mass number	36	39	40	40
Neutrons in nucleus	18	20	21	22

(a) Write down the atomic numbers of the four atoms.

(b) Which of the four atoms are isotopes of the same element?

(Answers on page 85)

We end this section by revising a shorthand way of showing the composition of an isotope.

Isotopic symbols

You may already have met a shorthand description of an atom; the mass number is shown as a superscript before the symbol and the atomic number as a subscript. In this way, $^{27}_{13}Al$ is a description of the aluminium atom. To make sure that you can use this convention correctly, try the next exercise.

Exercise 8 (a) Use your data book* to identify the stable isotopes of the following elements:

(i) Ar (i) Cu (iii) Si

Describe each one, using isotopic symbols.

(b) Write down the number of neutrons in the nucleus of each isotope.

(Answers on page 86)

*If you haven't used your data book to look up information about isotopes before, try either 'isotopes, stable, abundance' or 'nuclide, abundance' in the index. Abundance means the percentage of an isotope that occurs in nature and nuclide is a general word used to refer to any atom or ion having a particular nucleus.

In the next section, we look at the mass spectrometer and how it can be used to find the relative atomic masses of elements with several isotopes.

THE MASS SPECTROMETER

In the first Unit, you learned how to calculate relative atomic mass on the carbon-12 scale. In this section, you find out how relative atomic mass can be measured using a mass spectrometer. These instruments are also important for measuring the relative molecular masses of compounds, particularly organic ones, and determining their molecular structure.

Objectives. When you have finished this section, you should be able to:

(6) describe the principal parts of a mass spectrometer and explain their functions;

(7) explain how the deflection of a beam of ions by a magnetic field depends on the masses and the charges of the ions.

If the ILPAC videotape 'Instrumental Methods' is available, you should now watch the section on the mass spectrometer. Don't spend time viewing the whole tape at this point; your teacher will guide you to the appropriate section.

Whether or not you view the videotape, you should now go on to read about the mass spectrometer.

Look up 'mass spectrometer' in your text-book and read the section on it, bearing in mind objectives 6 and 7. You may also come across 'mass spectrograph'. This instrument works on the same principle as the mass spectrometer - the only difference is the way in which the ions are detected. When you have finished the reading, do the next two exercises.

Exercise 9 (a) Make a copy of Fig. 3 which is a diagram of a mass spectrometer.

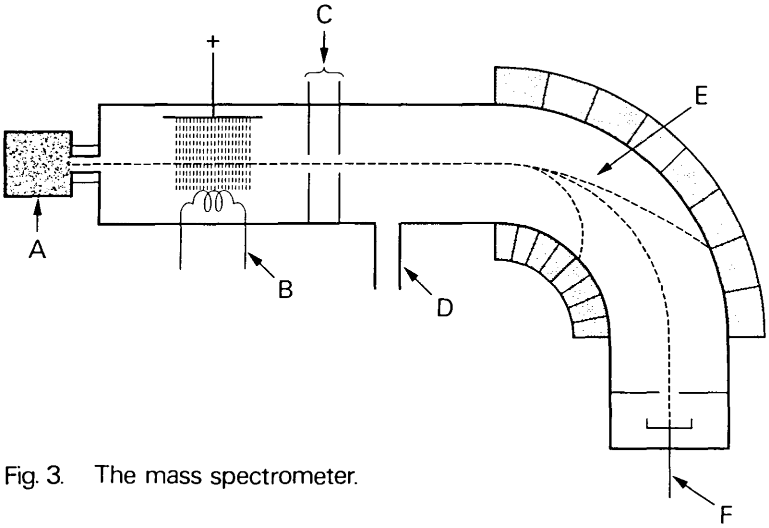


Fig. 3. The mass spectrometer.

(b) Label the parts A to F.

(c) Describe the function of, or process occurring in, each of these parts.

(Answers on page 86)

Exercise 10 The isotopic composition of the gas radon was investigated using a mass spectrometer, part of which is shown in Fig. 4 below.

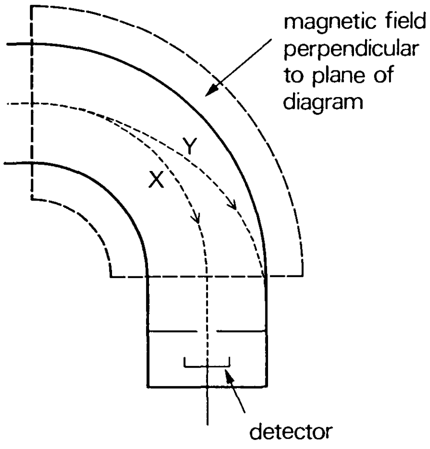


Fig. 4.

(a) Radon has two isotopes, $^{222}_{86}Rn$ and $^{220}_{86}Rn$.

(i) Write the formulae of the two singly-charged ions that would form in the instrument.

(ii) State which ion will follow the path marked X on the diagram.

(b) Mention two adjustments that could be made to the instrument to bring the ions from Y on to the detector.

(c) If Rn^{2+} ions were to form in the instrument, would you expect them to be deflected less than or more than the ions at X and Y?

(Answers on page 86)

Having established how a mass spectrometer works, we go on to interpret the information it records, known as a mass spectrum. You may also find the names 'mass spectrometer trace' or 'mass spectrogram' in your reading. These mean exactly the same. Spectrum is a Latin word and its plural is 'spectra'.

Interpreting Mass Spectra

Objective. When you have finished this section you should be able to:

(8) identify peaks on a simple mass spectrum and use them to calculate the relative abundances and masses of ions.

When a beam of ions strikes the detector in a mass spectrometer, it produces an electrical impulse, which is amplified and fed into a recorder. The mass of the isotope and its relative abundance are then shown by a peak on a chart. A set of such peaks is a mass spectrum.

Fig. 5 shows a mass spectrum for rubidium. The horizontal axis shows the mass/charge ratio of the ions entering the detector. If it is assumed that all the ions carry a single positive charge, the horizontal axis can also be labelled 'mass number', 'isotopic mass' or 'relative atomic mass'. The vertical axis shows the abundance of the ions. It can be labelled 'detector current', 'relative abundance' or 'ion intensity'.

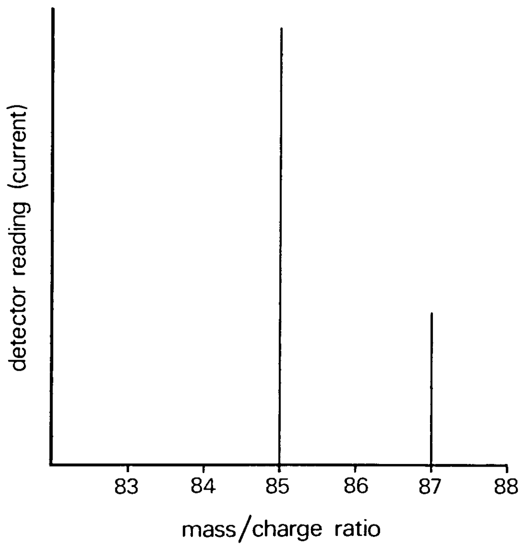


Fig. 5.

Exercise 11 Refer to Fig. 5 to answer this question.

(a) Describe the two isotopes of rubidium using isotopic symbols.

(b) What information do you get from the heights of the peaks on the mass spectrum?

(Answers on page 86)

In the next section we go on to use the information from mass spectra to calculate the relative atomic mass of an element.

Calculating relative atomic mass of an element

Objectives. When you have finished this section you should be able to:

(9) use a mass spectrum to calculate the relative atomic mass of an element;

(10) use percentage abundance data to calculate the relative atomic mass of an element;

(11) sketch a mass spectrum, given relevant data.

We start this section with a worked example, using the mass spectrum shown in Fig. 5. Read through it and then try the exercise which follows:

Worked Example Use Fig. 5 to calculate the relative atomic mass of rubidium.

W

Solution

1. Measure the height of each peak. The height is proportional to the amount of each isotope present.

   height of rubidium-85 peak = 5.82 cm

   height of rubidium-87 peak = 2.25 cm

   Therefore, the relative amounts of ^{85}Rb and ^{87}Rb are 5.82 and 2.25 respectively.

2. Express each relative amount as a percentage of the total amount. This gives the percentage abundance.

$$\%\text{ abundance} = \frac{\text{amount of isotope}}{\text{total amount of all isotopes}} \times 100$$

$$\%\text{ abundance of } ^{85}\text{Rb} = \frac{5.82}{5.82 + 2.25} \times 100 = 72.1\%$$

$$\%\text{ abundance of } ^{87}\text{Rb} = \frac{2.25}{5.82 + 2.25} \times 100 = 27.9\%$$

   The percentage abundance figures mean that for every 100 atoms, 72 are the ^{85}Rb isotope and 28 are the ^{87}Rb isotope.

3. Find the total mass of a sample of a hundred atoms.

$$\begin{aligned}\text{Total mass} &= ((85 \times 72.1) + (87 \times 27.9))\text{ amu*} \\ &= (6129 + 2427)\text{ amu} = 8556\text{ amu} \\ &= 8.56 \times 10^3\text{ amu (3 sig.figs.)}\end{aligned}$$

4. Find the average mass. This gives the relative atomic mass of rubidium.

$$\text{Average mass} = \frac{\text{total mass}}{\text{number of atoms}} = \frac{8.56 \times 10^{3}\ \text{amu}}{100} = 85.6\ \text{amu}$$

$\therefore$ relative atomic mass = $\boxed{85.6}$

*amu stands for atomic mass unit. 1 amu = 1.660 x 10^{-27} kg. This value was chosen because it is exactly one twelfth the mass of an atom of the carbon-12 isotope, which comprises 98.89% of natural carbon.

Now try a similar calculation for yourself by doing the next exercise.

Exercise 12 Use the mass spectrum shown in Fig. 6 to calculate:

(a) the percentage of each isotope present in a sample of naturally occurring lithium;

(b) the relative atomic mass of lithium.

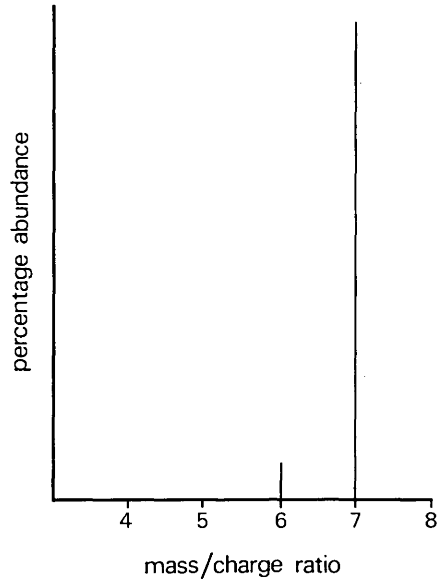


Fig. 6.

(Answers on page 86)

The next exercise is similar, but you are given data rather than a diagram of a mass spectrum.

Exercise 13 The mass spectrum of neon consists of three lines corresponding to mass/charge ratios of 20, 21 and 22 with relative intensities of 0.91; 0.0026; 0.088 respectively. Explain the significance of these data and hence calculate the relative atomic mass of neon.

(Answer on page 87)

You could also be asked to do the reverse of this type of problem - sketch a spectrum from percentage abundance data. Have a try at this by doing the next exercise.

Exercise 14 (a) Look up the percentage abundances of the stable isotopes of chromium.

(b) Sketch the mass spectrum that would be obtained from naturally occurring chromium. (Let 10.0 cm represent 100% on the vertical scale.)

(c) Calculate the relative atomic mass of chromium, correct to three significant figures.

(d) Label each peak on the mass spectrum using isotopic symbols.

(Answers on page 87)

You may be asked to calculate relative atomic masses directly from percentage abundance data, as you have just done in part (c) of Exercise 14. For more practice at this type of problem, turn to Appendix 3, page 84.

The relative abundances of different isotopes explain some anomalies that appear in the Periodic Table. Find out about them by doing the next exercise.

Exercise 15 When Mendeleev first devised the Periodic Table, he arranged elements in order of increasing relative atomic mass. In the modern version, elements are arranged in order of increasing atomic number.

(a) What would be the effect on the positions of

(i) tellurium and iodine,

(ii) argon and potassium,

if Mendeleev's system were reintroduced?

(b) How do you account for this effect? (Look up the relative abundances of the isotopes of $_{52}$Te and $_{53}$I; $_{18}$Ar and $_{19}$K.)

(Answers on page 87)

Now try the final exercise in this section which concerns a molecular element.

Exercise 16

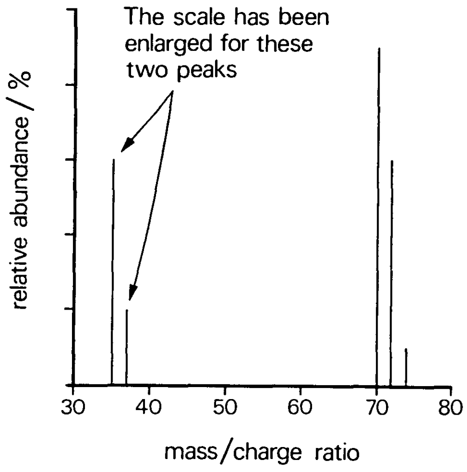


Fig. 7.

The element chlorine has isotopes of mass number 35 and 37 in the approximate proportion 3:1. Interpret the mass spectrum of gaseous chlorine shown in Fig. 7, indicating the formula (including mass number) and charge of the ion responsible for each peak.

(Answer on page 87)

The main use of mass spectrometry today is in identifying and analysing organic molecules which split up to give a great many different ions. We consider this aspect later in the course in one of the Units on organic chemistry.

Before we leave the mass spectrometer, we consider its use in explaining how the particles in a nucleus hold together.

Mass defect and binding energy

In this section we give a brief illustration of mass defect and binding energy to help you understand the size of the forces in atomic nuclei.

Objective. When you have finished this section you should be able to:

(12) calculate the mass defect of a nuclide, given appropriate masses in atomic mass units.

The mass spectrometer gives such accurate measurements that we now know the surprising fact that the mass of an atom is slightly less than the mass of its constituent parts. The next exercise gives you an example of this.

Exercise 17 Use Table 2 to calculate the relative atomic mass of a helium atom ($^{4}_{2}He$). Compare this with the measured value of 4.002598 amu.

Table 2

Particle	Mass/amu
proton	1.007 276
neutron	1.008 665
electron	0.000 548

(Answers on page 87)

The difference between the mass of a nuclide and the combined masses of its fundamental particles is known as the mass defect. The significance of the mass defect is shown by applying Einstein's famous equation describing the interconvertibility of mass and energy:

$$E = mc^2$$

where E = energy, m = mass and c = speed of light.

Image removed

Fig. 8. Albert Einstein 1879-1955

The energy corresponding to the mass defect, calculated using this equation, is known as the binding energy. A very small mass defect corresponds to a huge binding energy, because c^2 is such a large multiplying factor. The energy associated with the addition or removal of electrons is small by comparison, as you see in the next exercise, so that binding energy is essentially an indication of the very powerful binding forces holding the nucleus together. Indeed, both mass defect and binding energy are sometimes defined in terms of the nucleus alone.

Exercise 18 (a) Calculate the binding energy for one mole of helium atoms, using your answer to Exercise 17. (Hint: express the mass defect in kg and the speed of light in m s^{-1}, so that the energy is expressed in kg m^2 s^{-2}; you can easily convert tc J and kJ because 1 J = 1 kg m^2 s^{-2}.)

(b) The energy required to remove all the electrons from one mole of helium atoms is 331 kJ. What percentage of the binding energy is therefore associated with the electrons?

(Answers on page 87)

It has long been the dream of scientists to make the binding energy of the nucleus directly available for Man's use in a controlled way. We do use binding energy indirectly, of course, because it is released in nuclear reactions in the sun, where helium nuclei are formed by the fusion of hydrogen nuclei (i.e. protons).

From the last exercise, you can see that the fusion of four moles of hydrogen into one mole of helium releases approximately 2.7 x 10^9 kJ. By contrast, the combustion of four moles of hydrogen, a more conventional energy source, releases only 484 kJ. Clearly, there is plenty of energy available if only we can learn how to harness it.

Energy is not only associated with fusion processes but also, to a lesser degree, with fission, i.e. the splitting of nuclei. Some nuclei split up spontaneously releasing energy in the form of various types of radiation. We consider these unstable nuclei in the next section.

RADIOCHEMISTRY

Radiochemistry is the study of reactions involving changes in the nucleus which result in the emission of radiation (radioactivity). Many nuclei are unstable and disintegrate spontaneously, especially those of high atomic number; all known isotopes of elements where Z is equal to or greater than 83 are radioactive. In addition, there are radioactive isotopes of many lighter elements, and here the stability depends on the relative numbers of protons and neutrons.

We now consider the different types of radioactivity.

Types of radiation

Fig. 9.

You have probably seen the hazard warning sign for radioactive substances in a laboratory at school or college or in a hospital or factory. The danger lies in the fact that our bodies cannot detect radiation from a nucleus even though it can penetrate our bodies and damage their cells. Here we consider three types of radiation which can be emitted by nuclei of radioactive isotopes (radioisotopes).

Objectives. When you have finished this section you should be able to:

(13) describe the properties of alpha, beta and gamma radiation in terms of charge, mass and behaviour in a magnetic field;

(14) state the relative penetrating powers of alpha, beta and gamma radiation.

Read about the three types of radioactivity and their properties, listed in Objective 13, so that you can do the following exercises. Note that although the distinction between radiation and particles is rather an arbitrary one, as you will see later, we usually regard γ-radiation as an electromagnetic wave, and α and β emissions as particles.

Exercise 19 Fig. 10 shows how alpha and beta particles and gamma rays, emitted from a radioactive source, S, behave in an electric field.

(a) Use the information on the diagram to identify the type of emission present at P, Q and R.

(b) By what other means could a similar pattern of deflection of the three types of radiation be caused?

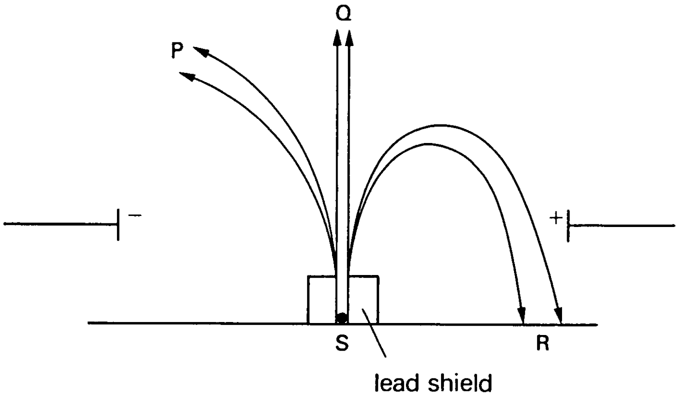


Fig. 10.

(Answers on page 88.)

Exercise 20 Copy and complete the following table to summarise the properties of alpha, beta and gamma emissions.

Table 3

Emission	Nature	Relative mass and charge	Symbol	Extent of deflection in electric or magnetic field	Relative penetration
alpha, α					
beta, β					
gamma, γ					

(Answers on page 88)

It is important for you to realise that the electrons in β-emission come from the nucleus. You consider this point in the next exercise.

Exercise 21 A nucleus consists of protons and neutrons and yet, during beta decay, it gives off electrons. Using isotopic symbols, write an equation to show how this is possible.

(Answer on page 88)

In the next section you apply your knowledge of alpha and beta particles to writing nuclear equations.

Nuclear reactions

Whereas chemical reactions leave the nucleus untouched and involve only the electrons surrounding it, nuclear reactions rearrange the particles within the nucleus. Also, different elements may be formed, in a process known as transmutation, which does not, of course, occur in chemical reactions.

We now examine some nuclear reactions and show you how to write equations for them.

Objectives. When you have finished this section you should be able to:

(15) complete and balance simple nuclear equations.

The basic nuclear reactions are alpha and beta particle emission, often called α and β decay. We go through the alpha decay in detail in the next worked example. Read through it and then do the exercise which follows.

Worked Example When thorium-228 decays, each atom emits one alpha particle. Write a balanced nuclear equation to show the process.

W

Solution

1. Write out the equation, putting in letters for the unknowns:

$$^{228}_{90}\text{Th} \rightarrow {}^{4}_{2}\text{He} + {}^{A}_{Z}\text{X}$$

In these equations, the atomic numbers and mass numbers of each side must balance; this allows you to calculate the unknowns, A and Z and X.

2. Find the atomic number of the new element, X, using the atomic numbers shown in the equation.

$$_{90}\text{Th} \rightarrow {}_{2}\text{He} + {}_{Z}\text{X}$$

$$90 = 2 + Z$$

$$Z = 90 - 2 = 88$$

3. Use a Periodic Table to identify the new element:

element with atomic number 88 is radium

$\therefore$ X = Ra

4. Find the mass number of the particular isotope of radium, using the mass numbers in the equation.

$$^{228}\text{Th} \rightarrow {}^{4}\text{He} + {}^{A}\text{X}$$

$$228 = 4 + A$$

$$\therefore A = 224$$

5. Write out the complete equation:

$$^{228}_{90}\mathrm{Th} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{224}_{88}\mathrm{Ra}$$

Note that ionic charges are not shown in nuclear equations. You may wonder, for example, why we do not write

$$^{4}_{2}\mathrm{He}^{2+}$$

In fact, the positive ions tend to pick up stray electrons and so the charges are usually omitted as a simplification. This also focuses attention on changes in the nucleus.

Now try some calculations yourself, by doing the next exercise:

Exercise 22 Write balanced nuclear equations to show the alpha decay of:

(a) $^{212}_{84}\mathrm{Po}$,

(b) $^{220}_{86}\mathrm{Rn}$.

(Answers on page 88)

You can adapt the method given in the last worked example to write an equation for β decay.

You may need to remind yourself of how the process takes place (see your answers to Exercises 20 and 21); then go on to try the next exercise.

Exercise 23 Write balanced nuclear equations to show the beta decay of:

(a) $^{212}_{84}\mathrm{Po}$,

(b) $^{24}_{11}\mathrm{Na}$,

(c) $^{108}_{47}\mathrm{Ag}$.

(Answers on page 88)

For further practice in writing nuclear equations, try the next exercise.

Exercise 24 Write the nuclear equations which represent:

(a) the loss of an α-particle by radium-226,

(b) the loss of a β-particle by potassium-43,

(c) the loss of an α-particle by the product of (b).

(Answers on page 88)

Finally, to summarise your knowledge of the effects of alpha and beta decay on the nucleus, do the next exercise.

<u>Exercise 25</u> What happens to the atomic number and the mass number of a nucleus when it emits:

(a) an α-particle,

(b) a β-particle.

(Answer on page 88)

Before we go on to consider the rate at which radioisotopes decay, we spend a short time considering nuclear stability. In other words, why do some nuclides decay and not others?

Nuclear Stability

<u>Objective</u>. When you have finished this section you should be able to:

(16) explain why certain nuclei are unstable, in terms of <u>neutron/proton ratio</u>.

Read about the stability of nuclei in your textbook. Look out for a diagram like Fig. 11 and read the passage that accompanies it.

To test your understanding of why certain nuclei are unstable, work through the following exercise, using Fig. 11, which shows the number of protons and neutrons in all stable nuclei, as a guide.

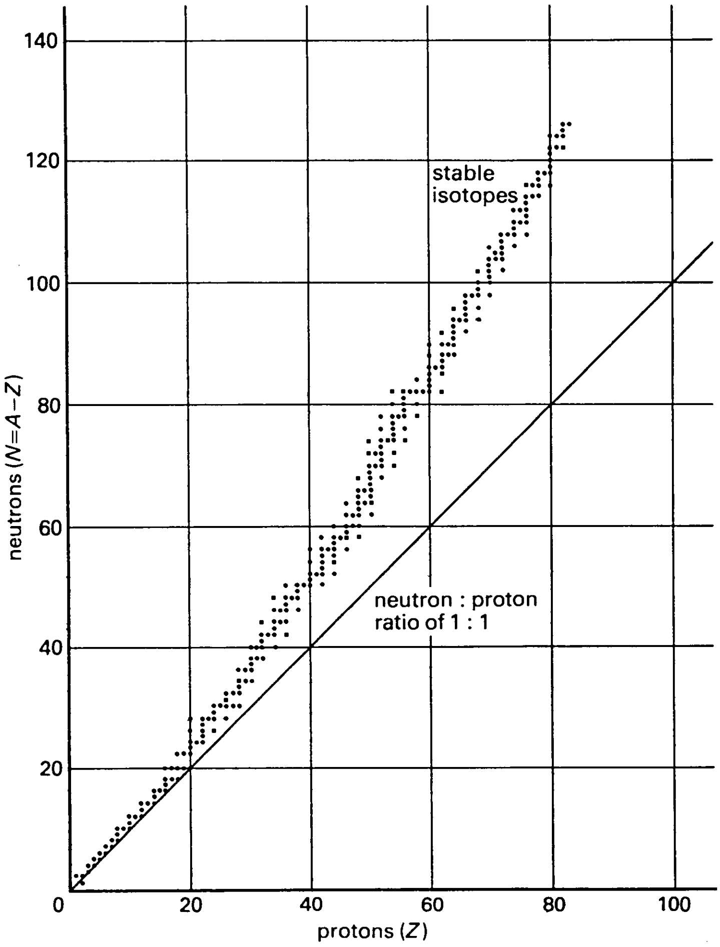


Fig. 11. Composition of stable nuclei

Exercise 26

(a) From the graph, identify the heaviest known stable nucleus, using isotopic symbols.

(b) Calculate the neutron to proton ratios (*N*/*Z*) for these stable nuclei:

(i) the nucleus identified in (a)

(ii) $^{108}_{48}$Cd   (iii) $^{12}_{6}$C

(c) Describe how the ratio *N*/*Z* for stable nuclei changes with increasing atomic number.

(d) By calculating *N*/*Z* ratios, predict whether the nuclei listed below are likely to be stable or unstable. Check your prediction against the graph.

(i) $^{11}_{6}$C   (iv) $^{143}_{56}$Ba

(ii) $^{60}_{30}$Zn   (v) $^{206}_{82}$Pb

(iii) $^{106}_{47}$Ag

(Answers on page 88)

To complete this section, try the following exercise.

Exercise 27 $^{14}_{6}$C is known to be a β emitter

(a) Write a nuclear equation for the emission.

(b) Work out the *N*/*Z* ratio for reactant and product nuclei.

(c) In view of the *N*/*Z* ratios, what can you conclude about the stability of reactants and products? Summarise the way β-emission changes the stability of a nucleus.

(Answers on page 88)

The decay of a single unstable nucleus is instantaneous and we cannot say when it will happen. However, we can measure the rate of decomposition (decay) of a sample containing many nuclei by counting the number of disintegrations which occur in unit time. In the next section, we look at the way in which the rate of decay varies with time.

THE RATE OF DECAY OF RADIOISOTOPES

The rate at which a particular radioactive isotope decays depends only on the amount present - it is unaffected by external factors such as temperature or pressure. In this section, we introduce the idea of half-life. This provides both a way to compare the rates of decay of different isotopes and, since no two isotopes have exactly the same half-life, a method of identification.

Objective. When you have finished this section, you should be able to:

(17) define the term half-life.

Read about half-life in your text-book. The term is used in connection with other reactions too, but you should concentrate on references to radioactive decay. We suggest you don't worry about a mathematical treatment at this stage - look for a graphical description. This should be sufficient to help you do the next two exercises.

Exercise 28

(a) Define the term 'half-life' as applied to a radioactive isotope.

(b) Why is it meaningless to speak of the 'total-life' of a radioactive isotope?

(Answers on page 88)

Exercise 29

(a) Use the following data to plot a decay curve for the transuranium element, americium-239.

Table 4

Mass of sample/g	time/hr
0.512	0
0.256	12
0.128	24
0.064	36
0.032	48
0.016	60
0.008	72
0.004	84
0.002	96
0.001	108
0.0005	120

Plot mass of sample on the vertical axis and time on the horizontal axis.

(b) What happens to the rate of a radioactive decay reaction, like this one, as it proceeds?

(c) How long would it take for the mass of americium to reach zero?

(d) Describe the shape that the curve would have if we had asked you to plot activity, in counts min^{-1}, rather than mass of sample.

(e) What percentage of the original activity remains after ten half-lives?

(Answers on page 89)

We now go on to consider an important application of the half-life of radioisotopes, radioactive dating.

Radioactive dating

Half-lives of certain radioactive elements have been used to calculate the age of rocks and estimate the age of the earth. In this section, we examine the use of carbon-14 in the dating of archaeological remains.

Objective. When you have finished this section, you should be able to:

(18) explain the use of the $^{14}_{6}C$ isotope in radiocarbon dating.

Read about radiocarbon dating in your text-book. Find out why the amount of $^{14}_{6}C$ in the atmosphere is constant and how archaeologists use this to find the age of objects from the past. We suggest that you do not concern yourself too much with the mathematical aspects at this stage, but you should be able to do simple calculations based directly on the concept of half-life, as in the next exercise.

Exercise 30 (a) Complete the following nuclear equation which shows how carbon-14 is formed from nitrogen-14 by the action of cosmic radiation:

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{A}_{Z}X$$

(b) Carbon from a piece of wood from a beam found in an ancient tomb gave a reading of 7.5 counts per minute per gram. New wood gives a reading of 15 counts per minute per gram. Estimate the year in which the tomb was built given that the half-life of $^{14}_{6}C$ is 5730 years.

(c) What is assumed to be constant over the period?

(Answers on page 89)

So far, we have described only natural radioactivity. In the next section we consider some of the nuclear reactions that have been carried out artificially.

ARTIFICIAL TRANSMUTATION OF ELEMENTS

All known elements heavier than uranium have been created artificially in the last fifty years. They are known as the transuranides, as they come after uranium in the Periodic Table. The most recently-discovered element, number 104, is the first transactinide, as it follows actinium in the Periodic Table but there are claims for the discoveries of elements 105 and 106. In this section, we look at various transmutation reactions.

Objective. When you have finished this section, you should be able to:

(19) write nuclear equations for reactions in which an element is bombarded by a neutron, proton, alpha particle or small nucleus.

Transmutation reactions are usually achieved by bombarding an element with a stream of particles. These may be neutrons, protons, alpha particles or small nuclei such as boron or carbon.

For example, if uranium-238 is bombarded with neutrons, it forms a new and unstable isotope, uranium-239

$$^{238}_{92}U + ^{1}_{0}n \rightarrow ^{239}_{92}U$$

in a reaction known as neutron capture. This unstable isotope then decomposes in two stages by beta decay. To see which new elements are formed, try the next exercise.

Exercise 31 Uranium-239 decays in two stages, by emitting beta particles. Write balanced nuclear equations to show which products are formed.

(Answers on page 89)

The next exercise is about the formation of another transuranide, curium.

Exercise 32 Complete the following nuclear equation to find out which nuclide, if bombarded with alpha-particles, changes to Cm-242.

$$^{A}_{Z}X + ^{4}_{2}He \rightarrow ^{242}_{96}Cm + ^{1}_{0}n$$

(Answer on page 90)

Now try the next two exercises which give you more practice in identifying the unknowns in equations for nuclear bombardment reactions.

Exercise 33 Work out the values of Z and A, and identify the symbols corresponding to X in the following equations.

(a) $^{16}_{9}F + ^{1}_{0}n \rightarrow ^{A}_{Z}X + ^{4}_{2}He$

(b) $^{17}_{8}O + ^{4}_{2}He \rightarrow ^{20}_{10}Ne + ^{A}_{Z}X$

(c) $^{15}_{7}N + ^{A}_{Z}X \rightarrow ^{12}_{6}C + ^{4}_{2}He$

(Answers on page 90)

Exercise 34 Work out Z, A and X in the following equations:

(a) $^{238}_{92}\mathrm{U} + ^{14}_{7}\mathrm{N} \rightarrow ^{A}_{Z}\mathrm{X} + 5^{1}_{0}\mathrm{n}$

(b) $^{246}_{96}\mathrm{Cm} + ^{A}_{Z}\mathrm{X} \rightarrow ^{251}_{102}\mathrm{No} + 8^{1}_{0}\mathrm{n}$

(c) $^{252}_{98}\mathrm{Cf} + ^{10}_{5}\mathrm{B} \rightarrow ^{A}_{Z}\mathrm{X} + 5^{1}_{0}\mathrm{n}$

(Answers on page 90)

Bombardment can also cause the break-up of a nucleus into smaller fragments. Try working out what happens when neutrons bombard uranium-235.

Exercise 35 Work out A, Z and X in the equation:

$$^{235}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n} \rightarrow ^{142}_{58}\mathrm{Ba} + ^{A}_{Z}\mathrm{X} + 2^{1}_{0}\mathrm{n}$$

(Answer on page 90)

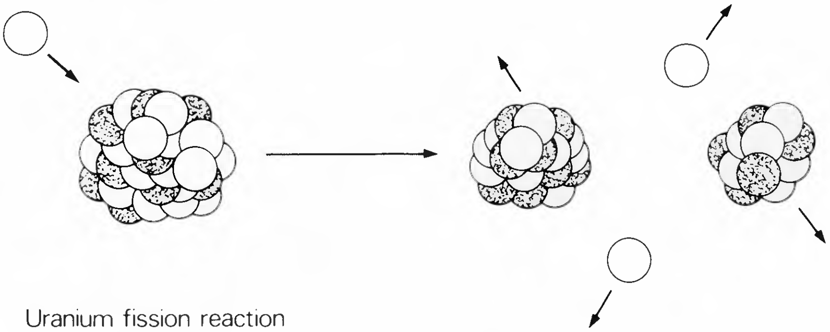
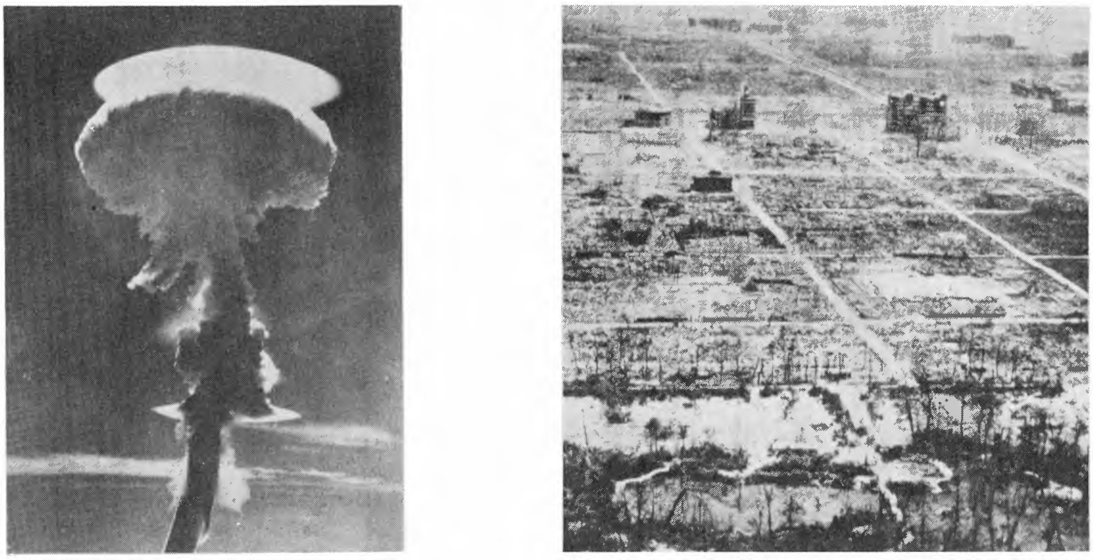


Fig. 12. Uranium fission reaction

This reaction, where the nucleus breaks into two roughly equal fragments, is called a fission reaction. In the process, some of the mass is lost from the uranium nucleus and transformed into a great deal of energy, which is set free.

Reactions like this are the basis of the nuclear power industry but have also been used for destructive purposes.......



Hiroshima, 1945

Fig. 13.

We have already mentioned one use of radioisotopes, in dating objects from the past. In this final section on radiochemistry, we suggest some reading on the many other uses of radioisotopes.

Uses of radioisotopes

Objective. When you have finished this section, you should be able to:

(20) state at least four ways in which radioisotopes are used and explain the principle behind each use.

Most text-books have a section covering the uses of radioisotopes. Look through a few books until you find one that gives a fairly detailed treatment. Among the uses to look out for are:

- atomic bombs
- nuclear reactors
- radiotherapy
- radiocarbon dating
- tracer techniques in biology and medicine
- thickness measurement

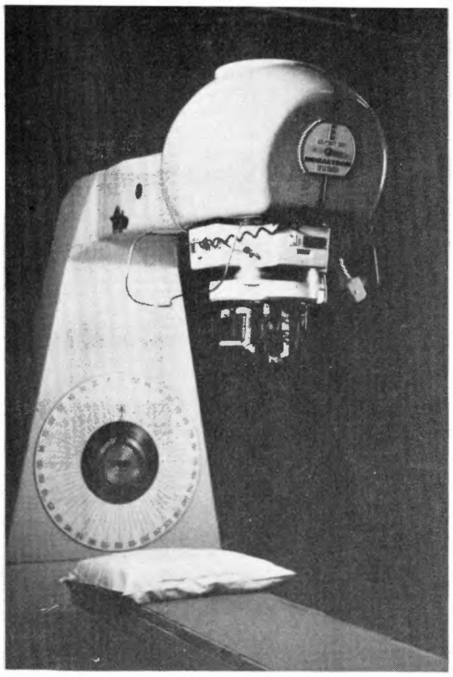


Fig. 14. Mobaltron cobalt unit

When you have read about the uses to which radioactive isotopes are being put, answer the following teacher-marked exercise:

Teacher-marked Exercises are designed to give you practice in essay-type questions. Before you start one, look back through your notes on the topic to make sure that you are clear about the main points. Next, read over the question carefully. Then, with all notes and text-books closed, make a short plan of your answer. Spend about half-an-hour writing and then hand your finished answer, together with your plan, to your teacher.

Teacher-marked Exercise — Choose three ways in which radioisotopes are used today. For each one, explain the underlying principle.

LEVEL ONE CHECKLIST

You have now reached the end of Level One of this Unit. The following is a summary of the objectives in Level One. Read carefully through them and check that you have adequate notes.

At this stage you should be able to:

(1) calculate the density of an atomic nucleus, given the nuclear volume, V_N;

(2) define the terms atomic number, Z and mass number, A;

(3) & (5) explain what isotopes are and use isotopic symbols to describe them;

(4) use values for atomic number and mass number to calculate the number of protons and/or neutrons in the nucleus;

(6) & (7) describe the principal parts of a mass spectrometer and explain how it works;

(8) identify peaks on a simple mass spectrum and use them to calculate the relative abundances and masses of ions;

(9) & (10) calculate the relative atomic mass of an element from (a) a mass spectrum, (b) percentage abundance data;

(11) sketch a mass spectrum, given relevant data;

(12) calculate the mass defect of an atom, given appropriate masses in atomic mass units;

(13) & (14) describe the properties of alpha, beta and gamma radiation;

(15) complete and balance simple nuclear equations;

(16) explain why certain nuclei are unstable, in terms of neutron/proton ratio;

(17) define the term half-life;

(18) explain the use of the $^{14}_{6}C$ isotope in radiocarbon dating;

(19) write a nuclear equation for a reaction in which an element is bombarded by a neutron, proton, alpha particle or small nucleus;

(20) state at least four ways in which radioisotopes are used and explain the principle behind each use.

LEVEL ONE TEST

To find out how well you have learned the material in Level One, try the test which follows. Read the notes below before starting.

1. You should spend about 1 hour on this test.
2. Hand your answers to your teacher for marking.

LEVEL ONE TEST

Questions 1 to 5 are either questions or incomplete statements followed by five suggested answers. Select the best answer in each case.

1. Which of the following statements about isotopes is FALSE?

A

A The presence of isotopes and their relative abundance in a sample of an element may be determined by a mass spectrometer.

B Isotopes of the same element have the same number of protons.

C Isotopes arise because different atoms of the same element have different numbers of neutrons.

D The existence of isotopes is a cause of non-integral chemical relative atomic masses of elements.

E Stable isotopes generally have more protons than neutrons. (1)

2.

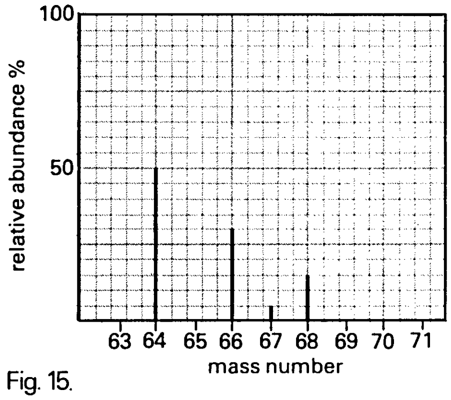


Fig. 15.

The graph shows the relative abundances of four isotopes of a certain element. Its relative atomic mass will be (to the nearest whole number)

A 64 D 67

B 65 E 68

C 66 (1)

3. The isotopic composition of a certain element X is 80% ^{24}X, 10% ^{25}X and 10% ^{26}X. The relative atomic mass of X is

A 25.00 B 24.67 C 24.33 D 24.30 E 24.25

A (1)

4. Archaeologists can determine the age of organic matter by measuring the proportion of $^{14}_{6}$C present. Assuming that carbon-14 has a half-life of 5600 years, a piece of wood found to contain $^{1}/_{8}$ as much carbon-14 as living material is calculated to have an age, in years, of

A

A 44 800 B 16 800 C 2 800 D 1 400 E 700 (1)

5. The NUCLEUS of $^{23}_{11}$Na contains

A

A 23 protons and 11 electrons

B 23 protons and 11 neutrons

C 11 protons and 12 neutrons

D 11 protons and 12 electrons

E 12 neutrons and 11 electrons (1)

In questions 6 to 8 inclusive, one, more than one or none of the suggested responses may be correct. Answer as follows:

A if only 1, 2 and 3 are correct

B if only 1 and 3 are correct

C if only 2 and 4 are correct

D if only 4 is correct

E if some other response, or combination, is correct.

6. In the nuclear reaction

$$^{43}_{20}\mathrm{Ca} + \mathrm{X} \rightarrow {}^{46}_{21}\mathrm{Sc} + \mathrm{Y}$$

the particles X and Y could be respectively

1. $^{2}_{1}\mathrm{H}$ and e^{-}
2. $^{4}_{2}\mathrm{He}$ and $^{1}_{1}\mathrm{H}$
3. $^{7}_{3}\mathrm{Li}$ and $^{4}_{2}\mathrm{He}$
4. $^{9}_{4}\mathrm{Be}$ and $^{7}_{3}\mathrm{Li}$

A

(1)

7. In the natural state the element M consists of the isotopes $^{28}_{14}\mathrm{M}$, $^{29}_{14}\mathrm{M}$ and $^{30}_{14}\mathrm{M}$ in the ratio 60:3:2 respectively. Correct statements about M in its natural state include that

1. the relative atomic mass is between 28.0 and 28.5
2. atoms of M each contain 14 electrons
3. atoms of M may contain 14, 15 or 16 neutrons
4. atoms of M each contain 14 protons.

A

(1)

8. The unstable nucleus $^{212}_{82}\mathrm{Pb}$ decays with β-particle emission, having a half-life of 10 hours. From this it follows that the

1. mass number of the product is 212
2. atomic number of the product is 81
3. fraction of the original isotope remaining after 20 hours is $\frac{1}{4}$
4. nucleus formed is stable.

A

(1)

For questions 9 and 10, choose an answer from A to E as follows:

A Both statements true: second explains first

B Both statements true: second does not explain first

C First true: second false

D First false: second true

E Both false

	First statement	Second statement	
9.	Gaseous isotopes of a given element, in ionic form, can be separated by passing them through a magnetic field.	Each particular isotope of a given element has the same number of protons and hence positive charges on the nucleus.	A (1)

10. The mass spectrometer CANNOT determine the relative molecular mass of organic compounds. | The mass spectrometer measures the masses of ions, not molecules. **A** (1)

11. (a) Explain what is meant by each of the following terms: **A**

(i) electron (iii) neutron

(ii) proton (iv) isotopes (4)

(b) The atomic number provides three pieces of information about an element. What are they? (3)

(c) The radioactive atom $^{224}_{88}Ra$ decays by α-emission with a half-life of 3.64 days.

(i) What is meant by 'half-life' of 3.64 days?

(ii) Referring to the product of the decay, what will be its mass number and its atomic number?

(iii) Radium is in Group II of the Periodic Table. In what Group will the decay product be? (4)

(d) Explain briefly the principles underlying

(i) the use of radioactive isotopes as 'tracers',

(ii) the dating of dead organic matter using radiocarbon, $^{14}_{6}C$. (6)

12. (a) Explain what you understand by the terms: **A**

(i) mass number (ii) relative atomic mass (2)

(b) Calculate the relative atomic mass of copper assuming it to contain 70% of ^{63}Cu and 30% of ^{64}Cu. (2)

(c) Briefly explain the principles of the use of the mass spectrometer for determining the mass number. (6)

(d) Complete the following equations

$$^{220}_{86}Rn \rightarrow {}^{216}_{84}Po \; +$$

$$^{214}_{82}Pb \rightarrow {}^{214}_{83}Bi \; +$$ (4)

(e) The activity of a sample of $^{222}_{86}Rn$ is reduced to 25% of its initial value after eight days. What is the half-life of $^{222}_{86}Rn$? (2)

13. A mixture of $^{2}_{1}H_2$ and $^{81}_{35}Br_2$ was analysed in a mass spectrometer. The following pattern of lines due to singly-charged ions was obtained. **A** part

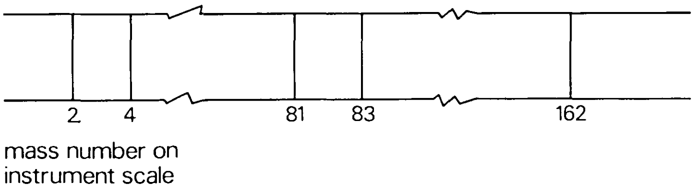


Fig. 16.

(a) State which ions give rise to each of these lines. (5)

(b) What apparent mass number would register on the instrument scale if the heaviest of these ions acquired a second charge? (1)

14. (a) Copy Table 5 and complete it by inserting properties of the three types of radioactivity.

SA

Table 5

	Relative charge	Relative mass
α		
β		
γ		

(3)

(b) Which of the types of radioactive emission has the greatest penetrating power, and which has the least? (2)

(c) Among the lighter elements, any isotope with a neutron/proton ratio greater than one is likely to emit radiation to bring the ratio closer to one.

(i) Write an equation for the decay of sulphur-35 by emission of a single particle.

(ii) Write down the neutron/proton ratios for the reactant and product nuclides. (4)

(d) Sulphur-35 has a half life of 88 days. How long will it take for a sample to decay to

(i) one quarter of its original activity,

(ii) zero activity? (2)

(Total 60 marks)

LEVEL TWO: ELECTRON ARRANGEMENTS

INTRODUCTION

Having considered the nucleus in Level One, we now move on to the electrons. We cannot 'see' electrons in a physical sense and yet chemistry is based on a description of where they are in an atom and how they move. Information about the arrangement of electrons has been obtained by 'disturbing' them, in two important ways:

(a) by bombarding them with streams of fast-moving particles and so detaching them from the atom;

(b) by forcing them into higher energy states and observing what happens when they return to normal.

Method (a) allows us to measure approximately the energy required to detach an electron, called the ionization energy; method (b) is the basis of emission spectroscopy and provides a better way of measuring ionization energies.

The study of ionization energies helps us to understand how electrons are arranged around the nucleus and how they behave in chemical reactions.

IONIZATION ENERGY

In your study of the mass spectrometer, you saw in Level One how atoms lose electrons to become positively-charged ions. In this section we consider the energy change needed to bring about the process.

Objectives. When you have finished this section, you should be able to:

(21) define first ionization energy;

(22) describe how ionization energy is measured by electron bombardment;

(23) calculate ionization energy from the results of electron bombardment experiments.

Read the section on ionization energy in your text-book. Look in detail at the definition of first ionization energy, bearing in mind that it refers to atoms in the gaseous state. Skim the part on measuring ionization energy by electron bombardment, also called the electron impact method. This should prepare you for the next exercise and the experiment which follows it.

Exercise 36

(a) Define first ionization energy.

(b) Write an equation to show the first ionization of sodium.

(c) Use your data book to find a value for the first ionization energy of sodium.

(Answers on page 90)

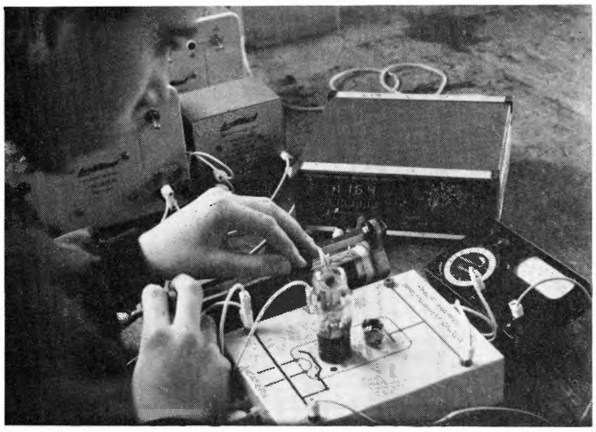
If it is available, you should now watch the ILPAC videotape 'Ionization Energy'.

If the videotape is not available, re-read the section on measuring ionization energy by the electron impact method in a text-book.

The next activity is an experiment to measure the ionization energy of argon by the electron impact method. The method is neither suitable for many elements nor very accurate but it does clarify the concept of ionization energy. In practice, the values quoted for ionization energy in data books have been obtained by emission spectroscopy, a method we shall cover at the end of this unit.

EXPERIMENT 1

Estimating the ionization energy of a noble gas



Aim

The purpose of this experiment is to estimate the ionization energy of argon by the electron impact method.

Introduction

Argon atoms can be ionized by bombarding them with high energy electrons:

$$\begin{array}{cccccccc} \text{Ar(g)} & + & e^- & \rightarrow & \text{Ar}^+\text{(g)} & + & e^- & + & e^- \\ & & \uparrow & & & & \uparrow & & \uparrow \\ & & \text{high energy electron} & & & & \text{electron from Ar} & & \text{bombarding electron with less energy} \end{array}$$

The process is carried out in an argon-filled radio valve, called a thyratron, as shown in Fig. 17.

The valve anode is kept at a negative potential to serve as a collector of positive ions. Note that the term 'anode' is not really appropriate here as an anode is normally positively charged.

The grid is kept positive to attract electrons emitted from the heated cathode.

The heater provides energy which allows the cathode to give off electrons.

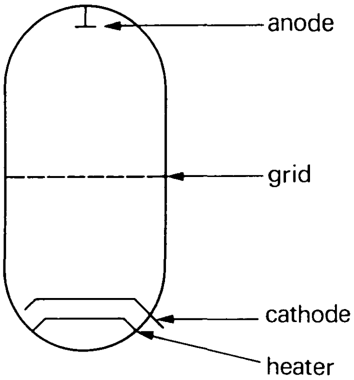


Fig. 17

The experiment takes place in several stages which we now illustrate with diagrams of the valve:

1. The cathode is heated (by passing a current through the heater circuit) and emits electrons. These are attracted towards the positively-charged grid, increasing their speed and energy. Some electrons are collected by the grid, while some pass through holes and move towards the anode. Since the anode is negatively charged relative to the grid, it repels electrons which turn back from it and return to the grid.

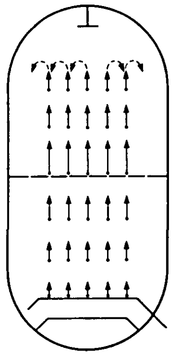


Fig. 18.

2. As the potential between the grid and the cathode is increased by adjusting a variable resistor, the electrons passing through the grid increase in energy but still cannot reach the anode. Note that the lengths of the straight arrows in Figs. 18 and 19 indicate their relative speeds.

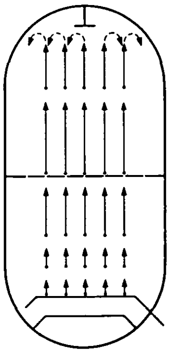


Fig. 19.

3. When the electrons have enough energy, they knock other electrons off the argon atoms, forming positive argon ions. These argon ions are then attracted to the negative anode where they pick up electrons from the circuit and cause a current to flow. This is registered by a milliammeter and marks the potential at which ionization takes place.

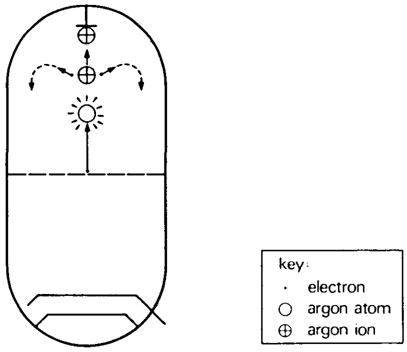


Fig. 20.

In brief then, the potential between the grid and the cathode is slowly increased until there is a rapid jump in the current shown by the milliammeter. This is the potential at which ionization takes place and we can calculate ionization energy from it.

Requirements

circuit board with labelled sockets for valve and connecting leads
argon-filled valve, type 884
power supplies
  (a) 6.3 V (AC or DC) for the cathode heater
  (b) 3 V (DC) for the anode circuit
  (c) 25 V (DC) for the grid circuit
potential divider, 250 Ω } these may be included in the circuit board
protective resistor, 200 Ω }
voltmeter, 25 V, high resistance
microammeter, 100 µA (0.1 mA)
12 connecting leads

Procedure

1. Insert the valve and connect the 6.3 V supply to the sockets labelled 'cathode heater'. Switch on to allow the valve to warm up for a minute or two.
2. Connect the voltmeter, microammeter and 3 V supply to the appropriate labelled sockets. Make sure the valve anode is negative with respect to the cathode, as shown in Fig. 21. (In most valve applications, the anode is positive, as the name implies.)

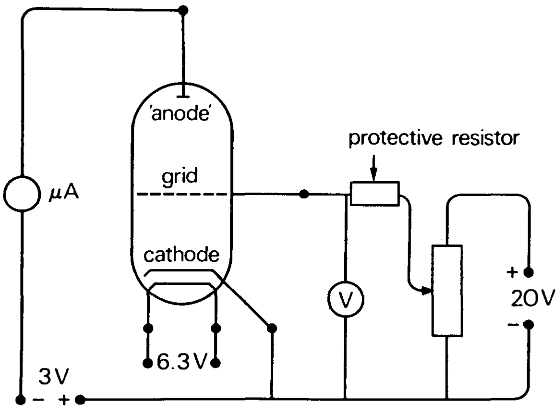


Fig. 21.

3. Set the potential divider to give the minimum accelerating potential; connect the 25 V supply and the protective resistor, as shown in Fig. 21. If you are not sure about these connections, check with your teacher.
4. Slowly increase the potential and watch the voltmeter. At the same time, watch the microammeter, which should read zero until ionization occurs.
5. As soon as the microammeter needle begins to move, note the voltmeter reading and reduce the potential to zero.
6. Repeat steps 4 and 5, this time looking for two additional indications of ionization:
   (i) a sudden decrease in the voltmeter reading (due to the surge in the grid current),
   (ii) a small purple glow in the valve (looking down from the top).

You may need to move the potential divider control a little further to see these effects, but always return it to zero as soon as possible to avoid damage to the valve.)

Calculation

One mole of electrons, on moving through a potential difference of one volt, acquires 96.3 kJ of energy*. To calculate the ionization energy of argon, multiply your voltage by this factor.

1st ionization energy of argon = _____ V x 96.3 kJ mol^{-1} V^{-1}

= _____ kJ mol^{-1}

Note that if you compare the value you have just calculated with the data-book value, you will probably find it is up to 20% higher. This can be explained by the limitations of the experimental method. The experiment is designed to give you an idea of the meaning of ionization energy, rather than to provide an accurate method of determining it. We will consider the more accurate method, based on emission spectra, towards the end of the Unit.

*The derivation of this factor is quite simple, but not important here. We have covered it in Appendix 2 to this Unit, page 83 .

Question

1. If another microammeter were included in the circuit for this experiment, between the grid and the protective resistor, it would show a current flowing throughout the experiment, rising suddenly after ionization.

   (a) Explain why a current flows before ionization.

   (b) Suggest one reason for the sudden increase after ionization.

(Answers on page 90)

Now try the following exercise to test your understanding of the electron impact method.

Exercise 37 In an electron bombardment experiment, a series of readings of current and potential was obtained and plotted as shown in Fig. 22.

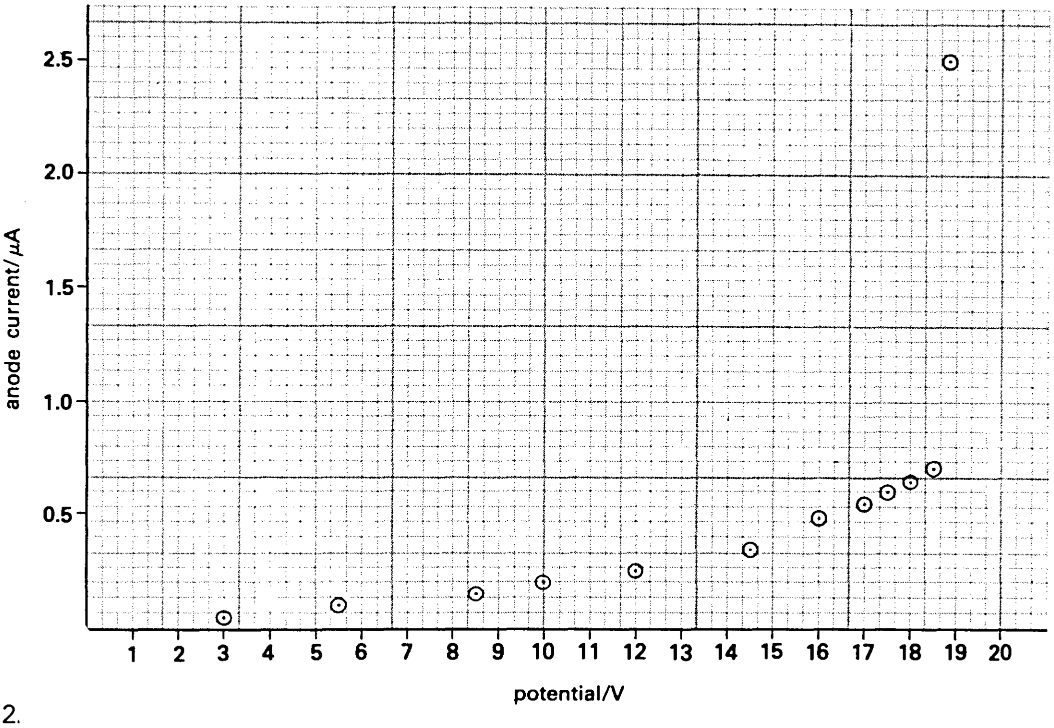


Fig. 22.

(a) Use the graph to estimate a value for the potential at which ionization occurs. Use a ruler to extend the vertical part of the curve until it crosses the horizontal axis. This is known as 'extrapolation'.

(b) Calculate the ionization energy to which this value corresponds.

(c) Using another valve, containing krypton, ionization occurred at 14.0 V. Calculate the corresponding ionization energy in kJ mol^{-1}.

(Answers on page 90)

Now that you know what the first ionization energy of an element is and how it can be measured, we turn our attention to the removal of more electrons from an atom and consider successive ionization energies.

Successive ionization energies

If you repeated the electron bombardment experiment with more robust apparatus and continued to increase the accelerating potential after the first ionization had occurred, there would be a further sudden increase in current. This would indicate the removal of a second electron. The energy change corresponding to this potential could be worked out in the same way and would give the second ionization energy for argon.

Theoretically, the bombardment process could go on until all the electrons were removed but, in practice, successive ionization energies have been obtained from spectroscopic measurements. We consider this method later in the Unit. In this section we concentrate on the definitions of successive ionization energies.

Objective. When you have finished this section, you should be able to:

(24) write equations representing second, third and subsequent ionization energies of a given element.

The important point about ionization energies after the first one is that an electron is removed from a positively charged ion each time. To make sure you understand this idea, try the next exercise.

Exercise 38 (a) Write equations to show the first, second and third ionization energies of aluminium.

(b) Would you expect the values of these ionization energies to increase or decrease, in the order: 1st, 2nd, 3rd?

(c) Explain your answer to (b).

(Answers on page 90)

Now we go on to consider how successive ionization energies give information about the arrangement of electrons.

Ionization energies and the arrangement of electrons

In this section you use successive ionization energy values for a specific element and find that they provide evidence for the arrangment of electrons around the nucleus.

Objectives. When you have finished this section, you should be able to:

(25) deduce the electronic arrangement of an element from a graph of $\log_{10}$ ionization energy against number of electron removed;

(26) use a graph of successive ionization energy against number of electron removed to provide evidence for the existence of subshells.

In the next two exercises, you examine successive ionization energy data for calcium and draw conclusions about its electron arrangement.

Exercise 39 (a) For the element calcium, plot $\log_{10}$ (I.E.) against the number (one, two, three ...) of the electron removed.

Table 6

Number of electron removed	Ionization Energy (I.E.) /kJ mol^{-1}	Log_{10} (I.E./kJ mol^{-1})
1	590	2.77
2	1145	3.06
3	4912	3.69
4	6474	3.81
5	8145	3.91
6	10496	4.02
7	12320	4.09
8	14207	4.15
9	18192	4.26
10	20385	4.31
11	57048	4.76
12	63333	4.80
13	70052	4.85
14	78792	4.90
15	86367	4.94
16	94000	4.97
17	104900	5.02
18	111600	5.05
19	494790	5.69
20	527759	5.72

(b) What information does this graph give about the electron configuration of the calcium atom?

(c) Why were you asked to plot $\log_{10}$ (I.E.) and not just ionization energy?

(d) Explain why the ionization energy increases when electrons are successively removed from a given shell.

(Answers on page 91)

This exercise fits the Bohr planetary model of the atom with which you are familiar. The large jumps in the value of the ionization energy indicate shells of different energies. You probably used a diagram like one of those shown in Fig. 23 to represent the structure of the calcium atom.

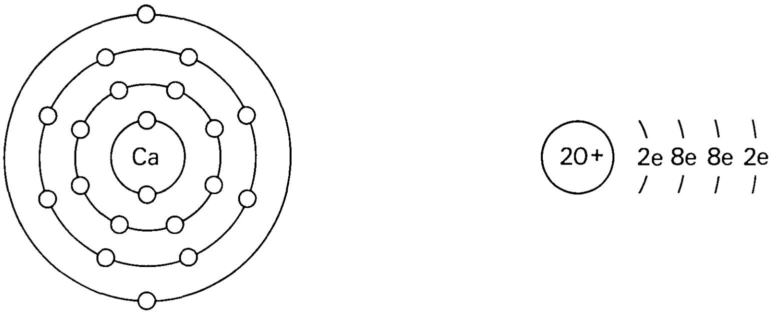


Fig. 23.

However, we now take a closer look at the ionization energies of electrons in a given shell, and find that this picture is oversimplified. There is evidence for a structure within each shell. To find out what this is, go on to do the next exercise.

Exercise 40 (a) From the data given in Exercise 39, plot a graph of ionization energy (not $\log_{10}$(I.E.)) against the number of electrons removed for electrons 3 to 10.

(Let 1 cm = 1000 kJ mol^{-1} on the vertical axis and 1 cm = 1 electron removed on the horizontal axis.)

(b) In the previous exercise, you learned that large jumps in ionization energy represent electrons being removed from different energy shells. What is your conclusion about the small jump which occurs between the eighth and ninth electrons?

(c) In view of your answer to (b), suggest how electrons are arranged in the second shell.

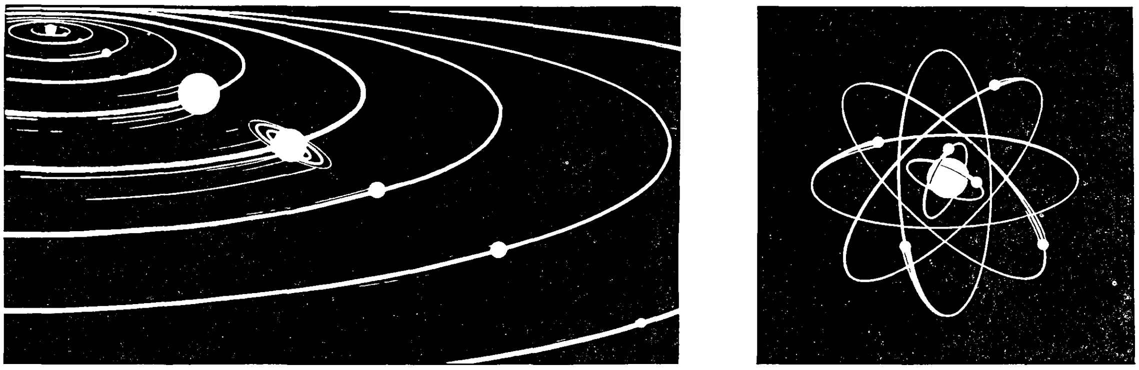
(Answers on page 91)

This exercise has shown you the shortcomings of the Bohr planetary model of the atom. But does this mean that the Bohr model is completely useless? We now pause to consider models in general before going on to a more sophisticated picture of the atom in the next section.

Models and their usefulness

You are probably more familiar with the term 'model' to describe a scaled-down version of an everyday object, such as a model car. But model cars differ enormously in the accuracy and detail with which the original is reproduced. At one extreme is the miniature replica, identical in every feature, including an engine, which burns fuel and moves the car along. Less refined is the familiar 'Dinky toy' model, which is recognisable in many details as a particular make of car, but has no working parts. Even less refined is the sort of model an architect might use for a new town centre plan - a solid, car-shaped block, to give an impression of the relative sizes of road and car. Finally, at the other extreme, there is the model a motorist would use after a car accident - just a rectangle on a map to indicate where the vehicle was at the time of impact.

None of these models is strictly 'correct' but each has its own use in a given situation. In a similar way, there are several models of the atom - from the solid sphere of John Dalton to the planetary model of Rutherford and Bohr with electrons as particles circling a central nucleus in fixed orbits.



(a) The solar system

(b) Planetary model of the atom

Fig. 24.

A further model, the orbital model, which we are going to use in the rest of this Unit, treats electrons as waves.

As we move more deeply into the subject, we meet increasingly detailed and sophisticated descriptions of atomic structure. But must we therefore discard earlier descriptions as 'wrong' and useless? In fact, there is no need to do so. For many purposes, such as explaining the states of matter, there is no point in using anything more complicated than the simple 'billiard ball' picture; in other cases, the planetary model is all that is needed. At A-level, you will continue to use the simple electron shell model, for example, to explain ionic compound formation.

Scientific theories are rather like models: they can be simple or elaborate, depending on the job they have to do. It is usually more sensible to ask, not whether a model is 'right' but whether it is useful. This is an important underlying theme in chemistry (and in science generally) and we shall return to it from time to time.

Before considering the orbital model of the atom as such, we spend a short time on the nature of electrons.

Wave-particle duality

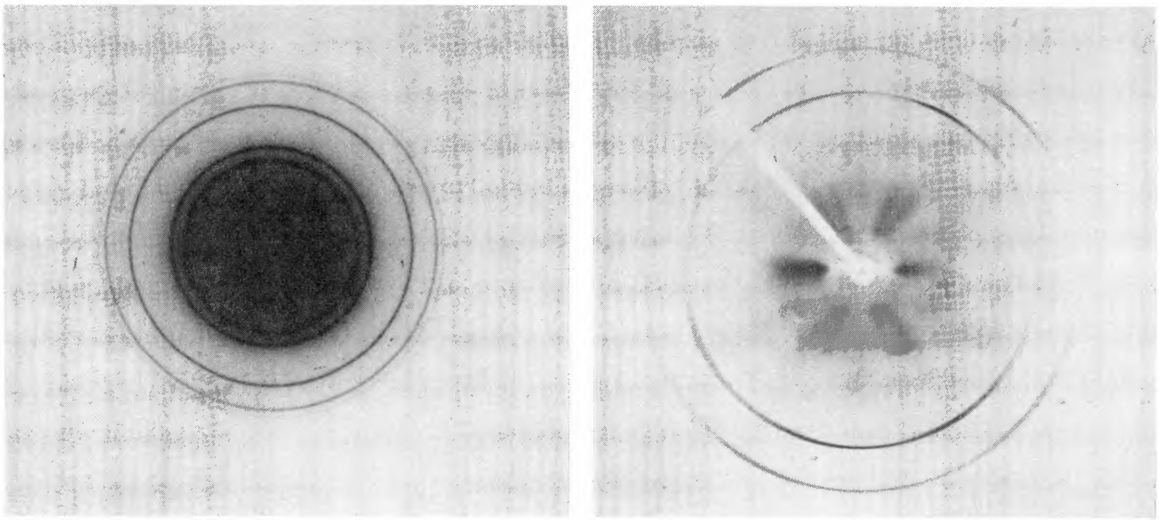
Until now, it has been convenient to think of electrons as minute, almost massless particles, but there is evidence to suggest that they also behave as waves.

Objective. When you have finished this section, you should be able to:

(27) describe briefly what is meant by the wave-particle duality of an electron.

Electron beams can behave like beams of light. For example, they can be diffracted, and diffraction is a property of waves. Read about the evidence which shows that electrons can behave as waves. Try 'electron diffraction' or 'electron, wave nature' in the index.

Fig. 25(a) shows an electron diffraction pattern obtained by passing a beam of electrons through aluminium foil. Notice the similarity to Fig. 25(b) which is the pattern obtained by passing X-rays through aluminium foil.



(a) (b)

Fig. 25. Diffraction patterns for aluminium produced by electrons (left) and X-rays (right)

Clearly then, we need more than one model for the electron. To explain some properties, we regard electrons as particles; to explain others we regard them as waves. In other words, they appear to have a dual nature. This phenomenon is known as 'wave-particle duality'.

It was by treating electrons as waves and applying to them mathematical methods, known as wave mechanics, that scientists came up with pictures of electron distribution. We go on to consider this model, where electrons do not occupy fixed orbits as in the planetary model, but orbitals, which describe how their charges are spread out in small regions of space.

THE ORBITAL MODEL OF THE ATOM

The main distinction between the planetary and orbital models of the atom is that, while the planetary model assumes that electrons keep to fixed orbits around the nucleus, the orbital model is based on the probability of finding an electron in a certain volume of space.

Objectives. When you have finished this section, you should be able to:

(28) give a simple, non-mathematical description of an orbital in terms of probabilities;

(29) draw the shapes of an *s*-orbital and a *p*-orbital;

(30) state the maximum number of electrons that an orbital can hold.

Look up 'orbitals' in a text-book and read the section on atomic orbitals. At this stage, ignore references to other sorts of orbital, such as molecular, metallic, bonding and anti-bonding orbitals. You need not worry about a mathematical treatment of orbitals.

An important point to bear in mind as you do your reading is the close relationship between the energy of an electron and its distance from the nucleus. As you saw from the successive ionization energy data, the further an electron is from the nucleus, the less energy is needed to strip it away from the atom. Outer electrons are at higher energy levels, less strongly attracted by the charge on the nucleus and, therefore, easier to remove.

In your reading, you may also come across the phrase 'quantum shell' used for energy shell. It arises from the Quantum Theory which, when applied to electrons in atoms, says that the electron can only exist in certain definite energy states. These energy states are called quantum shells.

Orbitals

As an extra help in picturing an orbital, we now include a short analogy. Read through this before attempting the exercise which follows.

Imagine that you were able to take a large number of photographs of a hydrogen atom (which you are not), containing one electron. By superimposing these photographs, you would obtain an impression of where the electron spends most of its time. The picture you would get would be something like Fig. 26.

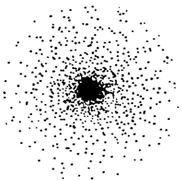


Fig. 26 Hydrogen atom 'charge cloud'

The picture is itself an over-simplification since it is restricted to two dimensions. The complete model is three-dimensional and spherical. Since even the two-dimensional picture is tedious to draw, we often use instead a boundary round the region where the probability of finding an electron is high - about 98% - as shown in Fig. 27. The space enclosed by this boundary is often called a probability envelope, or an orbital. At a more advanced level, you may have to make a mathematical distinction between probability envelopes and orbitals, but we shall regard them as the same, in common with most A-level text-books.

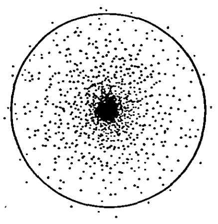


Fig. 27 Orbital boundary superimposed on charge cloud

Exercise 41 In the planetary model of the atom, we say that the electron has a definite energy and a definite position in space. How does the orbital model differ from this?

(Answer on page 92)

How many electrons per orbital?

In case you did not answer this question in your reading, we suggest you work it out for yourself, by doing the next exercise.

Exercise 42 The number of orbitals in a quantum shell is given by n^2, where n is the number of the shell. Use your knowledge of the total number of electrons in a shell to work out how many electrons a single orbital can hold.

(Answer on page 92)

Not all orbitals are spherical like the one shown in Fig. 27. In the next section, we look at some other shapes as well.

The shapes of orbitals

There are four types of orbitals whose shapes have been worked out, using wave mechanics. They are referred to by letter: *s*, *p*, *d* and *f*. These are the initial letters of the words 'sharp', 'principal', 'diffuse' and 'fundamental', originating from work carried out on the hydrogen spectrum which led to our present-day view of shells and sub-shells. You need only remember the initial letter.

You should be familiar with the shapes of *s* and *p* orbitals and we include *d* orbitals for interest, but *f* orbitals are too complex to show on a two-dimensional page.

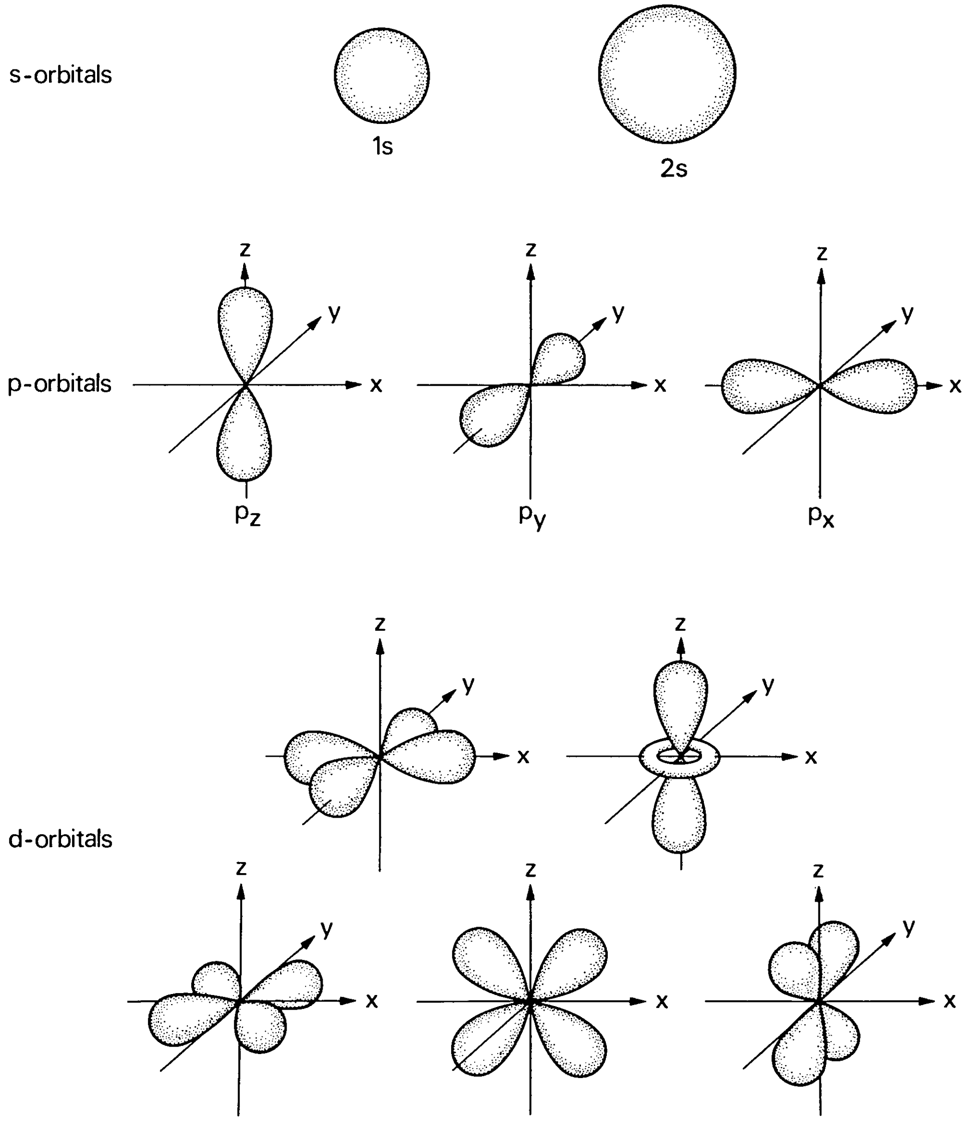


Fig. 28. The shape of s; p, and d orbitals

Study Fig. 28 which shows the shapes of *s*, *p* and *d* orbitals as predicted by wave mechanical calculations. You should also return to the section on orbitals in your text-book and read descriptions of these shapes. Then do the next two exercises.

Exercise 43 Explain why *p*-orbitals are labelled 'p_x', 'p_y' and 'p_z'. (*d*-orbitals are also given labels, but as they are not straightforward we have omitted them.)

(Answer on page 92)

Exercise 44 (a) How many electrons can be held in

(i) an *s*-orbital,

(ii) a set of three *p*-orbitals?

(b) Use one word in each case to describe the shape of

(i) an *s*-orbital, (ii) a *p*-orbital.

(Answers on page 92)

In the next section, we go on to consider how many orbitals of each type there are in each electron shell.

The number and type of orbitals in an electron shell

Each shell has a certain number of orbitals associated with it. In this section, we list these and you calculate the total number of electrons in a shell.

Objectives. When you have finished this section, you should be able to:

(31) state which orbitals are present in the first four electron shells;

(32) write down the order in which orbitals are filled in the first four electron shells.

The maximum number of electrons a shell can contain is given by $2n^2$, where n is the number of the shell. Use this expression in the exercise which follows to work out the total number of electrons in a shell.

Exercise 45 Table 7 gives the orbitals associated with the first four electron shells. Copy the table and fill in the last two columns to check the sum of the electrons in the separate orbitals against the total in each shell.

Table 7

Shell	Number and type of orbitals	Maximum number of electrons in each set of orbitals	Maximum number of electrons in the shell
First shell	one *s*		
Second shell	one *s* three *p*		
Third shell	one *s* three *p* five *d*		
Fourth shell	one *s* three *p* five *d* seven *f*		

(Answers on page 92)

In the next section, we go on to consider the order in which orbitals are filled. First, you need to know something about their different energy levels. Fig. 29 shows the orbitals in the first four shells for a typical light element, as well as some orbitals from the fifth to seventh shells. Each orbital is represented by a square box, □. The vertical axis represents energy and is roughly to scale. Note, however, that the energies vary from element to element, and even the order of energy levels may be different for heavier elements (see ILPAC Unit I5: Transition Elements).

Study Fig. 29 and then do the exercise which follows.

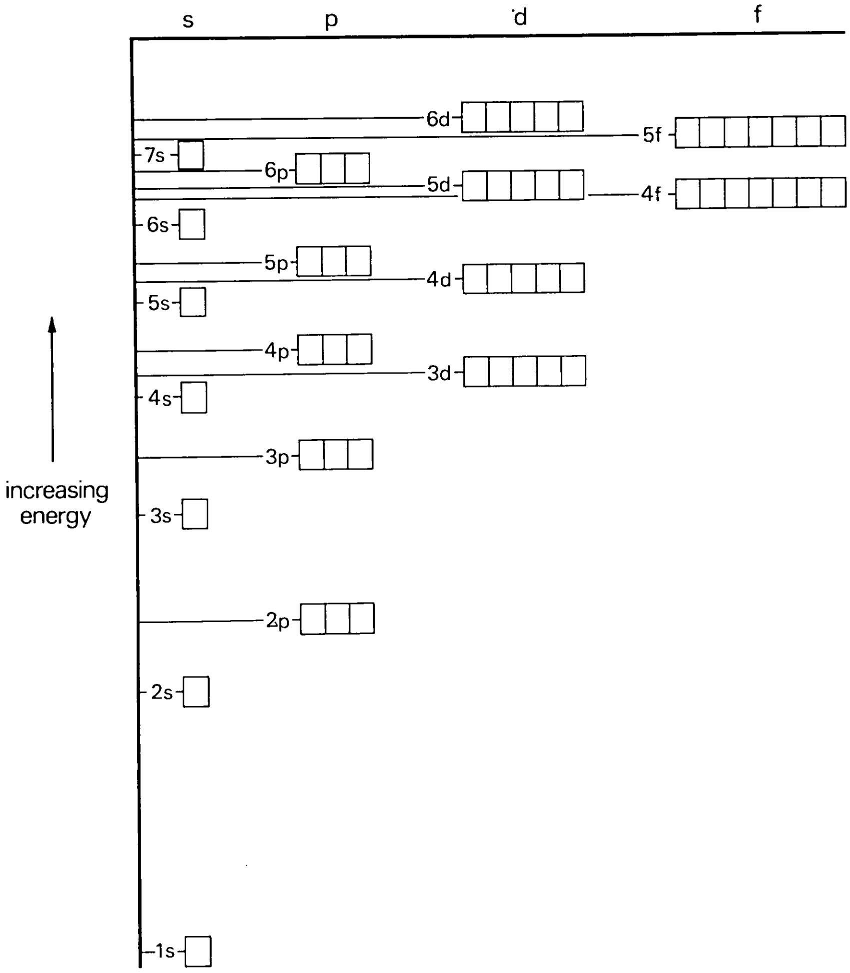


Fig. 29.

Exercise 46 Use Fig. 29 to list the first ten sub-shells in order of increasing energy.

(Answer on page 92)

In an atom, the orbitals are filled in order of increasing energy, starting from 1*s*. An aid to remembering this order is to write down the orbitals in columns, as shown below.

7*s*	7*p*	6*d*	
6*s*	6*p*	5*d*	5*f*
5*s*	5*p*	4*d*	4*f*
4*s*	4*p*	3*d*	
3*s*	3*p*		
2*s*	2*p*		
1*s*			

The order is then given by drawing diagonal lines through the symbols, as in Fig. 30.

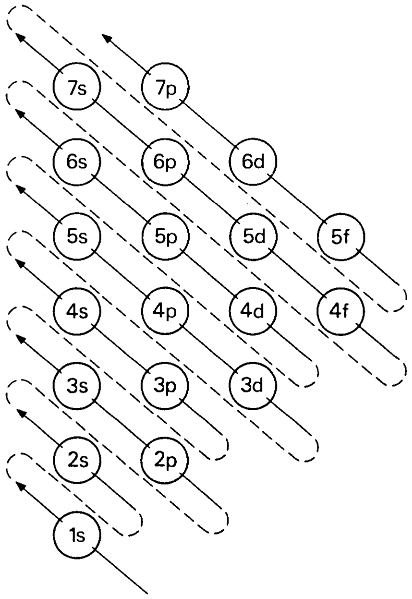


Fig. 30.

You are now ready to study the way in which electrons fill the available orbitals in an atom.

The arrangement of electrons in orbitals

We shall start with hydrogen, the simplest element, which has a single electron in the lowest energy orbital, the 1*s*. Then we go through the elements in order of increasing atomic number, imagining the addition of an extra electron each time.

This process is known as the aufbau*, or 'building-up' principle. As you go through it, the pattern of the Periodic Table emerges and we draw this together at the end of the section. We also introduce the conventional ways of writing out electronic configurations.

*Aufbau is a German word meaning to build up, pronounced 'owf-bow' (as in 'bow-wow').

Objectives. When you have finished this section, you should be able to:

(33) use the aufbau principle to work out the order in which orbitals are filled in a given element;

(34) express electronic configurations using

  (a) the electrons-in-boxes method;

  (b) *s, p, d, f* notation.

(35) write down the electronic configuration of any element or ion in the first four periods of the Periodic Table.

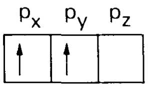
The aufbau principle

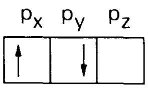
We now state three important rules which determine the order in which electrons occupy the vacant orbitals in an atom.

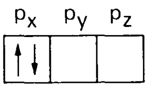
1. Of the available orbitals, the added electron will always occupy the one with the lowest energy.
2. Each orbital may hold only two electrons, and they must have opposite spin*. (Pauli exclusion principle.)
3. Where a number of orbitals of equal energy are available, the added electron will go into an empty orbital, keeping electron spins the same, before spin-pairing occurs. (Hund's rule.)

*Electrons can be thought of as spinning on an axis like the earth. Unlike the earth, however, which spins in only one direction, an electron can spin in either of two directions. The $\uparrow$ represents one direction of spin; the $\downarrow$ arrow the other. Furthermore, in any one 'box' when there are two electrons occupying it, they will spin in opposite directions. This is called spin-pairing and is shown as $\boxed{\uparrow\downarrow}$.

As an example of how Hund's rule operates, consider two electrons entering the *p*-orbital. There seem to be three possible arrangements.





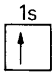


but the first is the only one which conforms to Hund's rule.

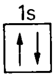
As an analogy, think of a double-decker bus in which passengers fill up the lower deck before climbing upstairs and in which, given the choice, passengers prefer to sit alone rather than share the seats.

We now apply the rules and work through the elements from hydrogen according to the aufbau principle.

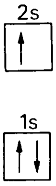
Hydrogen. The hydrogen atom contains one electron which therefore occupies the lowest energy orbital - the 1*s* orbital. The electron configuration is represented by:



Helium. The helium atom contains two electrons. Since the 1*s* orbital still has room for another electron, the second electron goes into it, and the configuration is:



Lithium. The lithium atom contains two 1*s* electrons and the third electron goes into the next orbital, i.e. the 2*s* orbital. Hence the electron configuration is:



Notice that we always label the boxes. By now you should be able to work out what happens for the next four elements.

Exercise 47 Draw the electron configuration of beryllium.

(Answer on page 92)

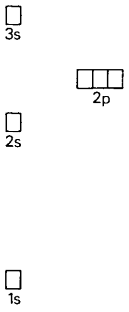
Exercise 48 Make three copies of part of Fig. 29 as shown, and draw in arrows to show the electron configurations of:

(a) boron,

(b) carbon,

(c) nitrogen.

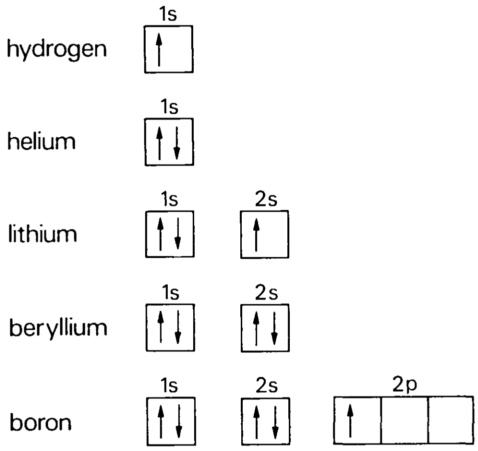
(Answers on page 92)



You can save time and space in writing down electron configurations by placing the orbital boxes in a row, as we now show.

Boxes-in-a-row

Obviously, on paper it is difficult to get the vertical spacings between energy levels right. However, the spacings are usually not critical and the boxes are most often placed side by side. We shall refer to this arrangement as 'boxes-in-a-row', or 'electrons-in-boxes'.



Remembering to label the boxes, do the next exercise:

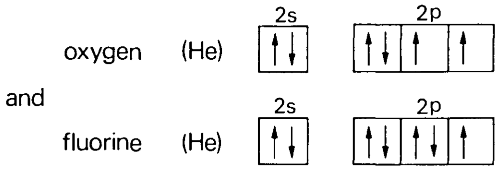
Exercise 49 Draw boxes-in-a-row to show the electron configurations of (a) carbon, and (b) nitrogen.

(Answers on page 92)

Now we look at a further simplification in writing down electron configurations.

Using a noble gas 'core'

The 'boxes-in-a-row' method can become tedious, particularly if the atom contains very many electrons. In any case, we are most often concerned with the outermost electrons in an atom - the inner 'core' is not involved in chemical reactions. Consequently, we can use a symbol for a noble gas to replace some of the arrows. This is possible for both the next two elements. Notice also that from this point on, electrons entering *2p* orbitals have to pair up with electrons which are already there. The electron configurations are therefore:



Now try this shorter method for the first two elements in the next period.

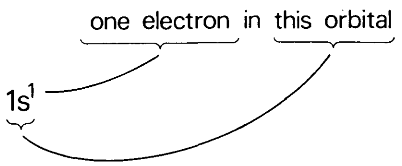
Exercise 50 Using boxes-in-a-row, and noble gas cores, draw diagrams to show the electron configurations of (a) sodium and (b) magnesium.

(Answers on page 92)

Another method of writing electron configurations does away with boxes altogether.

The s,p,d,f notation

In this method, the electron configuration of hydrogen is represented by -



Using this notation, the next three elements in the third period are:

aluminium	$1s^22s^22p^63s^23p^1$
silicon	$1s^22s^22p^63s^23p^2$
phosphorus	$1s^22s^22p^63s^23p^3$

and, of course, the noble gas core can be used here too:

aluminium	$(Ne)3s^23p^1$
silicon	$(Ne)3s^23p^2$
phosphorus	$(Ne)3s^23p^3$

Now do the next exercise in which you use this notation for the last three elements in this period.

Exercise 51 Use the *s,p,d,f* notation to write the electron configuration for

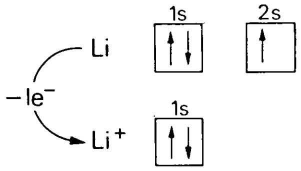
(a) sulphur,

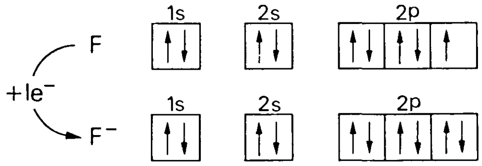
(b) chlorine,

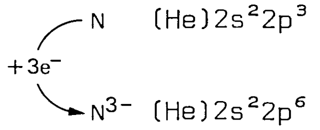
(c) argon.

(Answers on page 92)

The electronic configurations of ions derived from atoms can be represented in a similar manner. Here are three examples.







The next exercise gives you practice at writing electron configurations of ions.

Exercise 52 (a) Using the *s*, *p*, *d*, *f* notation, write the electron configuration of

(i) the oxide ion, O^{2-},

(ii) the magnesium ion, Mg^{2+}.

(b) Which element in the Periodic Table has the same electron configuration as these two ions?

(Answers on page 92)

In the fourth period, the pattern becomes more interesting. This is sometimes known as the first long period and we shall now see why. The electron configurations of the first two elements are straightforward. Work these out yourself, by doing the next exercise.

Exercise 53 Write the electron configurations of (a) the potassium atom and (b) the calcium atom, using the *s*, *p*, *d*, *f* notation.

(Answers on page 93)

Before you do the next exercise, look at the energy level diagram, Fig. 29. What does this tell you about the added electron in the next element, scandium?

Remember that an electron will always enter the orbital of lowest energy. Which has the lower energy - $3d$ or $4s$?

Also, you write out the orbitals in numerical order, not the order in which they are filled. Thus, the order from the third shell is:

$3s$ $3p$ $3d$ $4s$ $4p$ $4d$ $4f$ $5s$ ..... etc.

Exercise 54 Write the electron configuration of scandium using the s,p,d,f notation.

(Answers on page 93)

Scandium, therefore, differs from calcium by having one electron in the $3d$ orbital. Now, there are five equivalent $3d$ orbitals. Consequently, not just the scandium electron, but ten electrons can enter the third shell before it becomes necessary for them to go into the $4p$ orbital.

The series of elements:

Sc Ti V Cr Mn Fe Co Ni Cu Zn

represents this filling-up of the d orbitals. (We will return to this in the ILPAC Unit 'Transition Elements'.)

For an introduction to the electron configuration of this series of elements, try the next exercise:

Exercise 55 Write the electron configurations of

(a) the titanium atom,

(b) the vanadium atom,

(c) the iron atom.

In each case use

(i) electrons-in-boxes,

(ii) the s,p,d,f notation.

(Answers on page 93)

After zinc, electrons enter the $4p$ orbitals until, at krypton, these are full. To see how electrons fill in the rest of the fourth period, try the next exercise.

Exercise 56 Write the electron configurations of

(a) the gallium ion, Ga$^+$,

(b) the arsenic atom,

(c) the bromide ion.

In each case use

(i) electrons-in-boxes,

(ii) the *s*, *p*, *d*, *f* notation.

(Answers on page 93)

The fifth period starts with rubidium and strontium, very much like the fourth period. Then, with the 5*s* orbital full, electrons enter the 4*d* orbitals until these too are full. Finally, the 5*p* orbitals are filled.

In the next period, the pattern changes slightly. Look again at the energy diagram, Fig. 29. Use the information in the diagram to help you do the next exercise.

Exercise 57 Write down the orbitals which are filled in going across the sixth period.

(Answer on page 93)

The seventh period of the Periodic Table is similar, but incomplete.

You can now look at the Periodic Table as a whole and explain the major blocks into which it is divided. The Periodic Table shown in Fig. 31 is the 'long form' - to see why, compare it with other versions of the table. Study the table and use it to do the exercise which follows.

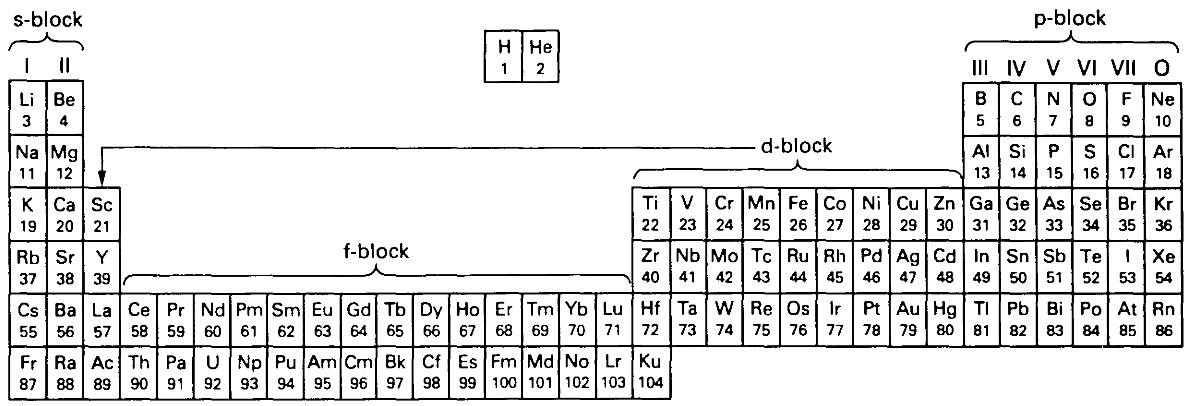


Fig. 31.

Exercise 58 (a) Explain why the *s*-block, *p*-block, *d*-block and *f*-block are so called.

(b) For the *s*- and *p*-block elements, the number of the last sub-shell to be occupied is the same as that of the period. Is this true of the *d*- and *f*-block elements? Give examples from Periods 4, 5 and 6.

(Answers on page 93)

In the next section, we return briefly to the topic of ionization energy.

USING IONIZATION ENERGY VALUES TO IDENTIFY AN ELEMENT

At the start of Level Two we used ionization energies as evidence for the shells and sub-shells in a calcium atom. You should also be able to reverse this process to identify an element from its ionization energy values.

Objectives. When you have finished this section, you should be able to:

(36) identify an element, given values of successive ionization energies.

The following exercise is part of an A-level question. Work through it to make sure that you can identify an element given $\log_{10}$ ionization energy.

Exercise 59 Here are the logarithms of all the successive ionization energies for a given element, X.

Table 8

Electron number	1	2	3	4	5	6	7	8
$\log_{10}$ (I.E.)	3.12	3.53	3.72	3.88	4.04	4.12	4.85	4.92

(a) Plot $\log_{10}$ (I.E.) against the number (first, second, third, etc.) of the electron removed.

(b) Write down the electronic configuration of this element using the *s*,*p*,*d*,*f* notation.

(c) To which group of the Periodic Table does the element belong?

(d) What is the formula of its ion?

(Answers on page 93)

You should also be able to identify an element by inspecting the successive ionization energy values and identifying the major 'jumps' or increases as changes of shell. The next exercise, which is part of an A-level question, gives you practice at this.

Exercise 60 The following table shows the first six ionization energy values for each of four consecutive elements in the Periodic Table.

Table 9

	Ionization energy/kJ mol^{-1}					
Element	First	Second	Third	Fourth	Fifth	Sixth
W	1260	2300	3800	5200	6500	9300
X	1520	2700	3900	5800	7200	8800
Y	420	3100	4400	5900	8000	9600
Z	590	1100	4900	6500	8100	10500

Which of the elements do you think

(a) is a noble gas,

(b) will form an ion with a single positive charge,

(c) will form an ion with a double positive charge?

(Answers on page 93)

At the end of the last section, you saw how the addition of one electron to each successive element gives rise to the Periodic Table. We now consider the pattern which emerges from the first ionization energies of successive elements.

First ionization energies of successive elements

If the first ionization energies of successive elements in the Periodic Table are plotted against atomic number, an interesting graph emerges.

Objectives. When you have finished this section, you should be able to:

(37) plot a graph of first ionization energy against atomic number;

(38) explain the term 'periodic' with reference to the plot of first ionization energy against atomic number;

(39) explain the changes in first ionization energy that take place across the second period.

Exercise 61 Plot a graph of first ionization energy against atomic number for the first twenty elements (i.e. up to Ca).

Label the vertical axis: '1st ionization energy/kJ mol^{-1}', and extend the scale from zero to 2500 (in intervals, say, of 500).

Label the horizontal axis: 'Atomic number' and extend the scale from zero to 20.

Obtain the necessary ionization energies from your data book. Label each point with the symbol for the element and join each point to the next by a straight line.

(Answer on page 94)

Your graph should clearly show a pattern for the elements of the second period (Li to Ne) which is repeated for those of the third period (Na to Ar).

There is a general increase along a period with discontinuities between Be (Z=4) and B (Z=5) and between N (Z=7) and O (Z=8) in Period 2. There are also discontinuities for the corresponding elements in Period 3.

Use your text-book to read about the changes in first ionization energy across a period. Look for an explanation in terms of:

1. the extent to which inner-shell electrons 'shield' the outer-shell electrons from attraction by the nucleus;
2. the difference in energy between *s* and *p* orbitals;
3. the difference between removing a paired electron and an unpaired electron;

Note that the so-called stability of half-filled orbitals is not, in itself, an explanation - it is part of the pattern which needs explaining!

Before you do the next exercise, look at Fig. 32. You will recognise that the first part of this graph corresponds to the one that you have drawn in Exercise 61. You will also see that the repeating pattern appears at higher atomic numbers: first ionization energy is a periodic property of the elements.

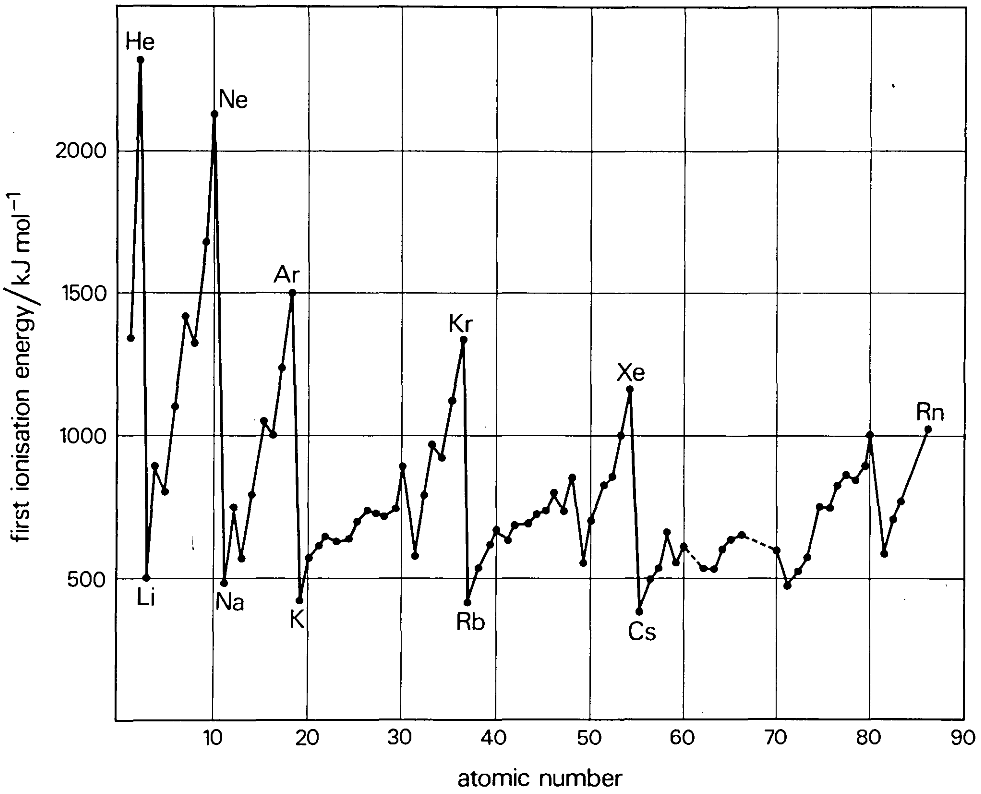


Fig. 32.

Now use Fig. 32 in order to do the next exercise.

Exercise 62 Explain the changes in first ionization energy

(a) between hydrogen and helium,
(b) between helium and lithium,
(c) between beryllium and boron,
(d) between nitrogen and oxygen,
(e) along the peaks, Fig. 32 (for the noble gases),
(f) along the lowest points (for the alkali metals).

(Answer on page 94)

At the beginning of Level Two, we mentioned two ways of disturbing an atom in order to find out about its electronic structure. We then dealt with the first of these - electron bombardment - and now we come to the second - emission spectroscopy.

EMISSION SPECTROSCOPY

You know that white light consists of a continuous range of wavelengths which we distinguish by colour. Fig. 33 shows a typical arrangement for producing a spectrum. Each line is an image of the slit caused by a particular wavelength of light. If there is a continuous range of wavelengths, the lines merge together into bands of colour in a continuous spectrum.

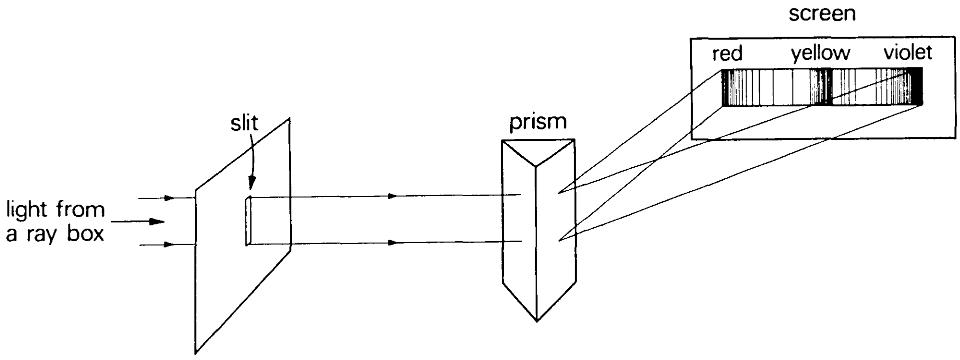


Fig. 33

Coloured light emitted from sources such as sodium street lamps, neon lights and coloured flames, generally consists of a mixture of a limited number of wavelengths. Emission spectroscopy is concerned with the examination of this sort of emitted radiation.

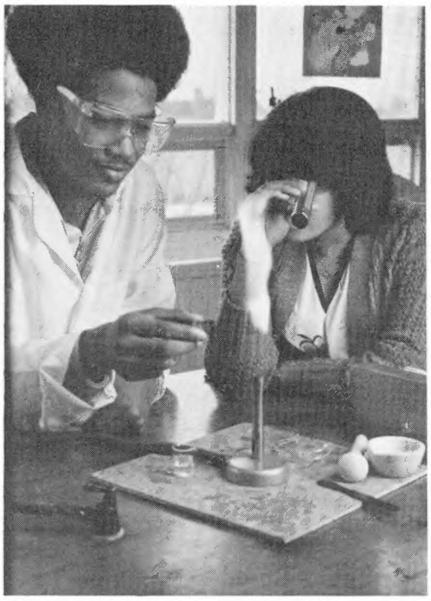
Objective. When you have finished this section, you should be able to:

(40) describe the difference between a continuous spectrum and a line emission spectrum.

We start this section with an experiment in which you see some common emission spectra for yourself.

EXPERIMENT 2

Using a hand spectroscope to observe the emission spectra of some *s*-block elements



Aim

This experiment is designed to give you a qualitative introduction to the spectra emitted by some *s*-block elements when their atoms are excited by heating samples in a Bunsen flame.

Introduction

You use a hand spectroscope to observe the continuous spectrum emitted by the tungsten filament of a light bulb. Using a flame test wire, you then obtain coloured emissions from some *s*-block elements, view these in turn through the spectroscope and compare them with the continuous spectrum from the tungsten filament.

We recommend that you work in pairs in this experiment. All three operations - preparing the flame test wire, obtaining a brightly-coloured flame and having the spectroscope ready to look at the flame for the few moments that it lasts - are fairly tricky and require practice and concentration. We suggest that one person prepares the flame while the other stands ready with the spectroscope. You can then change roles so that you both have a chance to observe each spectrum.

Requirements

fume cupboard with gentle fan
electric lamp with tungsten filament pearl light bulb
hand spectroscope
colour plate of spectra
Bunsen burner and bench protection sheet
flame test wire (or tongs and supply of filter paper)
hydrochloric acid, HCl, concentrated ---------------------- ✖
boiling tube or other glass container for hydrochloric acid
small pestle and mortar
spatulas
watch glasses
at least three of the following:
   barium chloride, $BaCl_2(s)$
   calcium chloride, $CaCl_2(s)$
   lithium chloride, $LiCl(s)$
   potassium chloride, $KCl(s)$
   sodium chloride, $NaCl(s)$
   strontium chloride, $SrCl_2(s)$

Hazard warnings

Hydrochloric acid has a vapour which irritates and can damage your eyes. Wear safety spectacles and work in the fume cupboard for this experiment.

Spectroscope. UNDER NO CIRCUMSTANCES must you look through this at the sun. If you do so, your eyes may be permanently damaged.

Procedure

1. Switch on the lamp and look at the bulb through the spectroscope. Look for a series of colours, one running into the next. This is a continuous spectrum. Compare what you see with the coloured plate showing the emission spectrum from a tungsten filament.

2. Hold the spectroscope up to a window which does not face the sun. You must NEVER point the spectroscope directly at the sun. This could result in permanent damage to your eyes.

   You should see the continuous spectrum of visible light.

3. Light the Bunsen burner - adjust it to get a roaring flame.

4. Dip the flame test wire into concentrated hydrochloric acid, then hold it in the hottest part of the flame. Repeat the process until there is little or no colour from the flame test wire in the flame. You may have to repeat this step several times, especially towards the end of the experiment, but certainly no more than twelve times.

5. Crush a little of the salt to be tested finely in a pestle and mortar and mix with a little concentrated hydrochloric acid on a watch glass. Be careful here - use just enough of the acid to give you a semi-solid 'mush' of crystals.

6. Dip the cleaned flame test wire into the mush of the salt to be tested. Adjust the flame until it is pale blue and hold the wire in it. Your partner should be standing by with the spectroscope and should now look through it at the flame. Look for brightly coloured lines.

   There are several lines for each element and it will probably not be possible to get them all into view at once. The yellow line in the sodium spectrum is easy to see and will probably persist through the spectra of all the elements you try. You can use this line to help you locate lines on the spectra of the other elements, by looking either to the right or left of it. Checking with the coloured plate of spectra will give you an idea of where to look for lines from a particular element.

7. Repeat steps 2-5 with the salts of at least two other elements. Also use the spectroscope on any other vapour lamps which may be available, including street lamps, if there is one in view from the laboratory.

Question

What is the difference between a continuous spectrum and a line emission spectrum?

(Answer on page 94)

Now that you have examined some spectra, we go on to explain why the coloured bands are produced.

Why do atoms emit light?

In this section, we consider what is happening when atoms give out light. This phenomenon is the basis of emission spectroscopy.

Objectives. When you have finished this section, you should be able to:

(41) explain the emission of light by atoms in terms of excited states;

(42) state the relationship between wavelength and frequency;

(43) state the relationship between energy and frequency of radiation (Planck's relationship).

The process that takes place when atoms of an element are given energy - by heating them in a Bunsen flame, for example, or by passing an electric discharge through a gas at low pressure - is summarised in Fig. 34.

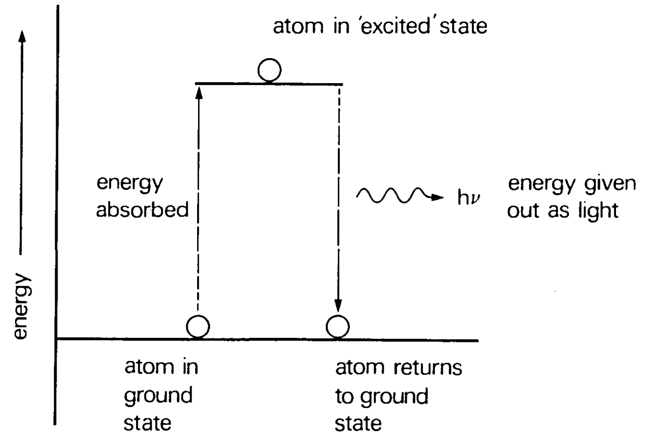


Fig. 34.

At room temperature, nearly all the atoms in a given sample of substance are in the ground state, i.e. the electrons occupy the orbitals of lowest energy.

In a flame, or other energy source, electrons move to orbitals of higher energy. The resulting excited states are not stable: each excited electron soon falls to a lower energy state and, in the change, a definite amount of energy, called a quantum, leaves each atom. The energy appears as radiation of a particular wavelength, which may be visible and coloured. The emission spectra you have been looking at consist of a series of coloured lines, each line corresponding to a particular energy drop, from a higher energy level to a lower one. The greater the number of electrons making a particular transition, the more intense the corresponding spectral line.

When you looked at ordinary daylight through a spectroscope, however, you saw a continuous spectrum. In other words, a beam of white light consists of a mixture of coloured beams. The different colours correspond to different values of wavelength, λ (Greek letter lambda). Fig. 35 indicates the approximate wavelength boundaries and the complete span (400 nm - 700 nm) is called the visible range.

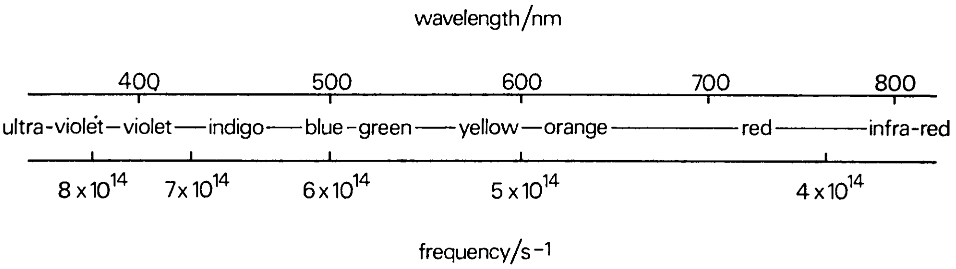


Fig. 35. Visible spectrum

Coloured beams can also be distinguished by their different frequencies. Frequency is represented by the symbol ν (Greek letter nu, pronounced 'new'). Study the diagram of the spectrum and use it to answer the following exercise:

Exercise 63 Using the information in Fig. 35, write the relationship between wavelength and frequency

(a) in words,

(b) as a mathematical statement.

(Answers on page 94)

The proportionality constant is the speed of light, c, so the equation linking wavelength and frequency is:

$$\lambda = \frac{c}{\nu} \quad \text{where } c \text{ is the speed of light } (2.998 \times 10^8 \text{ m s}^{-1})$$

All radiation is a form of energy, which can only be transmitted in discrete 'packets' called quanta. The energy of each quantum is proportional to the frequency of the radiation. Fig. 36 shows the complete electromagnetic spectrum (of which Fig. 35 represents just the central part). Study it for a few moments and then do the next exercise.

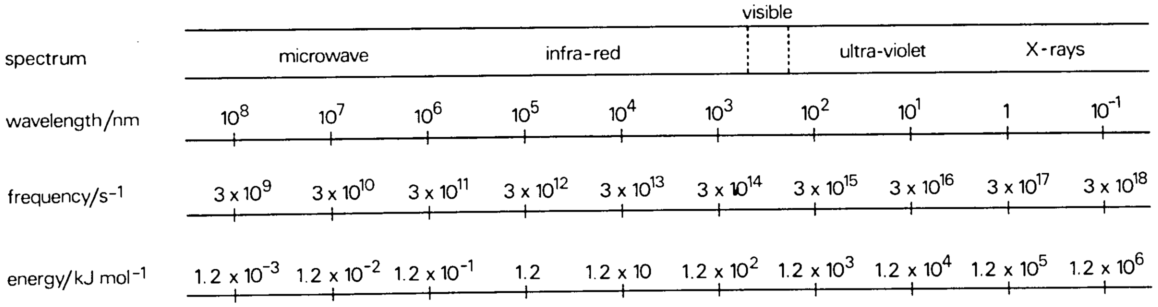


Fig. 36 Complete electromagnetic spectrum

Exercise 64 Explain why ultraviolet rays are more harmful to our skin than infra-red rays.

(Answer on page 94)

The relationship between a quantum of energy and the frequency is:

$$E = h\nu$$

where h = Planck's constant and ν = frequency of radiation.

This important relationship, often called Planck's relationship, has provided the key to finding out the differences between energy levels in atoms, as we shall see in the next section.

The visible part of the hydrogen emission spectrum

In this section, we examine the visible part of the hydrogen spectrum in detail and relate the energy of light emitted to the electron transitions taking place in the atom.

Objectives. When you have finished this section, you should be able to:

(44) calculate the frequency of a given form of radiation using the relationship $\lambda = c/\nu$;

(45) calculate the energy associated with a given form of radiation using Planck's relationship;

(46) explain how the energy of a line in the spectrum relates to the electron transition taking place in the atom.

The visible part of the hydrogen spectrum consists of a series of lines which get closer together at shorter wavelengths (higher frequencies). It is known as the Balmer series, after its discoverer. Fig. 37 is a diagram of the main lines in this series.

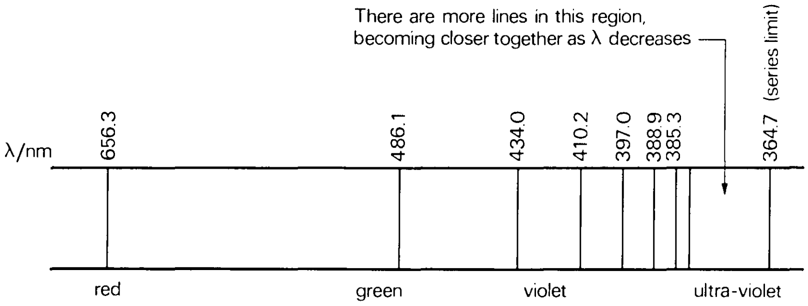


Fig. 37 The Balmer series

Use the information from Fig. 37 to do the next exercise.

Exercise 65 Using the relationship $\lambda = c/\nu$ and Planck's equation, calculate the energy of the red line in Fig. 37.

$h = 6.63 \times 10^{-34}$ J s

$c = 3.00 \times 10^{8}$ m s^{-1}

(Answers on page 95)

Planck's constant is sometimes quoted with reference to one mole of electron transitions, i.e. 3.99×10^{-13} kJ s mol^{-1}.

The energy you have just calculated is the energy needed to boost an electron from the second energy level to the third. It is given out as a quantum of light, called a photon, when the electron drops back to the second level. Fig. 38 shows this electron transition (n=3 to n=2) with its corresponding spectral line; in addition, it shows transitions from higher energy levels to the level n=2 and their corresponding spectral lines. At increasing frequencies, the lines get closer and closer until they merge.

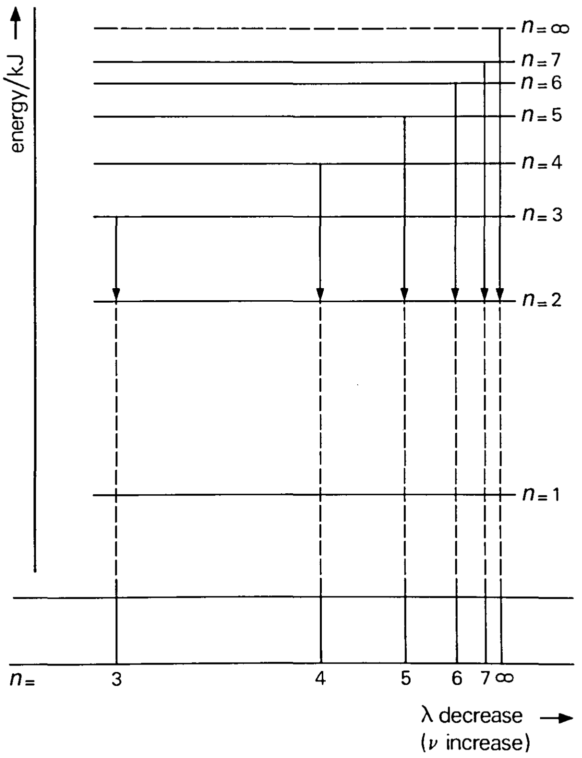


Fig. 38. Electron transitions and the Balmer series

Exercise 66 (a) What electron transition corresponds to the point where the spectral lines merge?

(b) What happens to the electron if $n = \infty$?

(c) Could you use the energy value at this point to calculate a value for the ionization energy? Explain.

(Answers on page 95)

In the next section, we go on to look at the other series in the hydrogen emission spectrum.

The complete hydrogen emission spectrum

In this section, we show that each series in the hydrogen spectrum corresponds to a set of electron transitions starting and ending at a different energy level. One of these series can be used to calculate ionization energy values.

Objectives. When you have finished this section, you should be able to:

(47) describe the emission spectrum of atomic hydrogen;

(48) sketch at least one series of lines from the hydrogen spectrum;

(49) explain how a hydrogen spectrum is produced.

If it is available, you should now watch the ILPAC videotape 'The hydrogen spectrum'.

Read about the emission spectrum of hydrogen in a text-book.

The essential piece of apparatus, a discharge tube, contains hydrogen at very low pressure. Look for a description of how a discharge tube is used and the changes that take place inside it.

If the apparatus is available, your teacher may set up a demonstration of the hydrogen emission spectrum for you. If so, you should view it through a hand spectroscope and try and identify some of the lines by comparing them with a photograph or Fig. 37.

The relationship between the various series of lines which go to make up the hydrogen spectrum is shown in Fig. 39. Each series is named after its discoverer. You do not need to learn all these names, but you will find it useful to remember Balmer and Lyman.

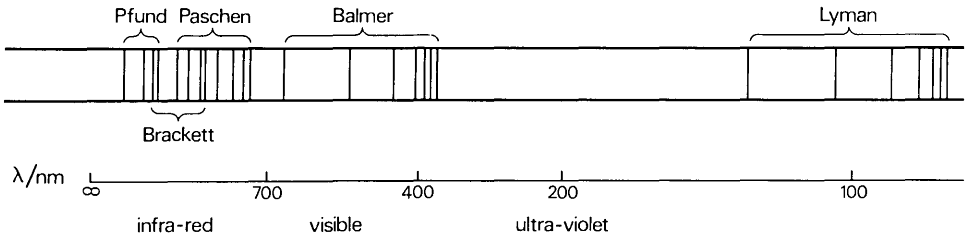


Fig. 39. The hydrogen spectrum

Study the diagram for a few moments and then use it to do the exercise which follows.

Exercise 67 (a) In what way are the other series in the hydrogen spectrum similar to the Balmer series?

(b) Give a simple explanation for this similarity, in terms of energy levels.

(Answers on page 95)

The pattern in the spectral lines has been described mathematically by the Rydberg equation:

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

where λ is the wavelength of the radiation in nm; R_H is a constant, the Rydberg constant. Its value for the hydrogen spectrum is 1.0967758×10^7 m^{-1}. n_1 and n_2 are integers, with the value of n_1 always being greater than n_2.

n_2 represents the electron shell to which the electron is dropping back and n_1 represents the electron shell to which the electron has been promoted. For a given series then, n_2 has a fixed value (in the Balmer series, $n_2 = 2$) and n_1 has a range of values, from ($n_2 + 1$) to infinity.

Fig. 40 below shows the relationship between the main series in the hydrogen spectrum and the energy levels with which they are associated.

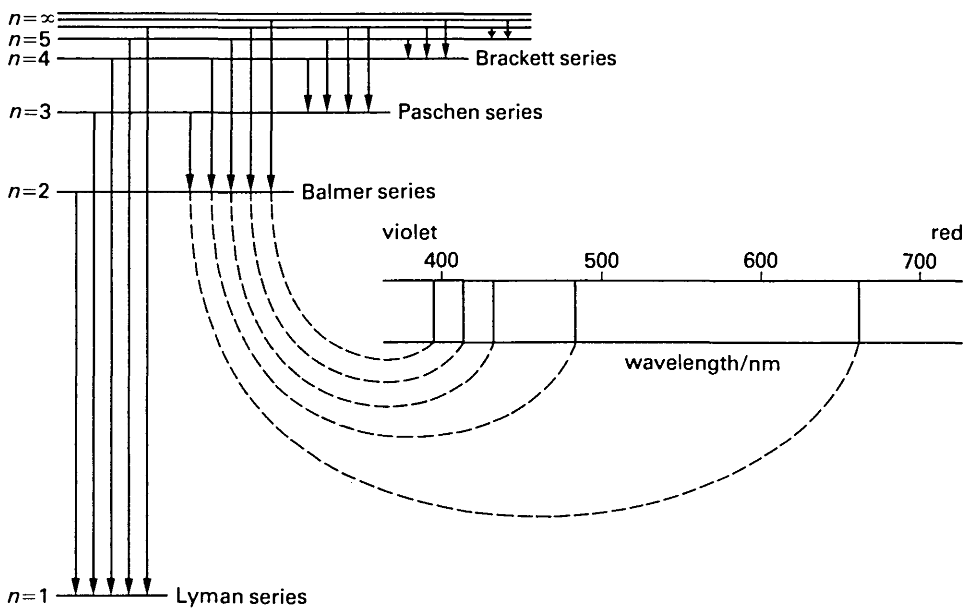


Fig. 40. Electron transitions and the hydrogen spectrum

Use the diagram to help you answer the next exercise.

Exercise 68 Which series of lines in the hydrogen emission spectrum would be suitable for determining its ionization energy Give a reason for your answer.

(Answer on page 95)

You may have been surprised that so far, in our study of the hydrogen emission spectrum, we have related the spectral lines to electron transition between major energy shells in the atom, without mentioning sub-shells. There is a good reason for this. In the hydrogen atom, there is no difference in energy between the sub-levels within a shell. However, in atoms other than hydrogen, the sub-shells are at different energy levels and we can easily demonstrate their existence by emission spectra.

In such multi-electron atoms, many electron transitions, from one orbital to another in different shells, or even within the same shell, are possible. These result in more complex emission spectra consisting of a great many lines.

It is possible to analyse a complex emission spectrum into a large number of converging series like those you have seen for hydrogen, but they are not so obvious because they overlap. At A-level, you will not be asked to interpret in detail anything more complex than the hydrogen spectrum.

In the final section of this Unit, we go on to see how the ionization energy of hydrogen can be calculated from frequency measurements of the appropriate series of lines in its emission spectrum. The ionization energy of any element can be calculated using a similar method, but since the details are more complicated, you need only know that it can be done in principle.

Convergence limits and ionization energy

You have noticed that the lines in each series in the hydrogen emission spectrum get closer and closer together at higher frequencies. We now make use of this fact to calculate the ionization energy for hydrogen.

Objectives. When you have finished this section you should be able to:

(50) explain what is meant by the convergence limit of a series of lines in the hydrogen emission spectrum;

(51) calculate a value for the ionization energy of hydrogen by obtaining the convergence limit graphically.

Read about convergence limits in the hydrogen spectrum and then do the following exercise.

Exercise 69 (a) Explain how the convergence limit of the Lyman series can be used to provide a value for the ionization energy of hydrogen.

(b) Why would the convergence limit of the Balmer or the Brackett series not be suitable for determining the ionization energy?

(Answers on page 95)

In the next exercise, we suggest graphical methods in which you can use the frequencies of radiation emitted in the Lyman series to calculate a value for the ionization energy of hydrogen.

Exercise 70 Table 10 shows the frequency of lines in the Lyman series in the emission spectrum of hydrogen. Complete the table and then use the information to obtain the first ionization energy of hydrogen by one of the methods below. We suggest you use method (ii) if your syllabus requires knowledge of the Rydberg equation.

Table 10

Energy level, n, of excited electron	Frequency, ν $/10^{15}\ \mathrm{s}^{-1}$	$\Delta\nu$ $/10^{15}\ \mathrm{s}^{-1}$	$\frac{1}{n^2}$
2	2.466	0.457	
3	2.923	0.160	
4	3.083		
5	3.157		
6	3.197		
7	3.221		
8	3.237		
9	3.248		

The symbol Δ (Greek letter 'delta') is used to refer to the difference between two values of a physical quantity. Thus, $\Delta\nu = \nu_2 - \nu_1$.

(a) EITHER

(i) Plot a graph of $\Delta\nu$ (vertical axis) against ν (horizontal axis). (You can use either the higher or the lower value of ν in each pair as long as you are consistent. Better still, plot two lines using both values in each pair.) Extrapolate the curve to $\Delta\nu = 0$ and estimate a value of ν at this point.

OR

(ii) Plot a graph of ν (vertical axis) against $1/n^2$ (horizontal axis). Extrapolate the line to $1/n^2 = 0$ (i.e. $n = \infty$) and estimate a value of ν at this point.

(b) Use Planck's constant to calculate a value for the ionization energy from this frequency. Hint: ionization energy refers to one mole of electrons.

(c) Compare the value you have calculated with the value given in your data book for the first ionization energy of hydrogen.

(d) If you used method (ii), explain how your plot relates to the Rydberg equation. Obtain a value for the Rydberg constant from the slope of the line and/or the intercept.

(Answers on page 95)

To help you draw together your ideas about the hydrogen spectrum and its use in determining the structure of the atom, do the Teacher-marked Exercise which follows. After you have looked through your notes, we suggest that you put them away and write your answer in examination conditions, allowing about half-an-hour.

✓

Teacher-marked Exercise

A

The atomic spectrum of hydrogen is given by the following relationship:

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

(a) (i) What does λ represent?

(ii) What do the terms n_1 and n_2 represent?

(iii) What are the units of the constant R_H?

(b) The spectrum comprises a number of lines which may be divided into a number of series.

(i) Why does the spectrum consist of lines?

(ii) Why is there a small number of series in the spectrum?

(iii) Explain why each series converges and in what direction it converges.

(c) What method is used to generate the light source for observing the atomic spectrum of hydrogen?

(d) Name the instrument used to resolve the hydrogen spectrum.

LEVEL TWO CHECKLIST

You have now reached the end of this Unit. Look again at the checklist at the end of Level One. In addition, you should be able to:

(21) define first ionization energy;

(22) & (23) describe how ionization energy is measured and calculated by an electron bombardment method;

(24) write equations representing second, third and subsequent ionization energies of a given element;

(25) deduce the electron arrangement of an element from a graph of $\log_{10}$ ionization energy against number of electron removed;

(26) use a graph of successive ionization energy against number of electron removed to provide evidence for the existence of subshells;

(27) describe briefly what is meant by the wave-particle duality of an electron;

(28) give a simple, non-mathematical description of an orbital in terms of probabilities;

(29) draw the shapes of an *s*-orbital and *p*-orbital;

(30) state the maximum number of electrons that an orbital can hold;

(31) to (33) use the aufbau principle to work out the order in which orbitals are filled in a given element;

(34) to (35) write down the electronic configuration of any element or ion in the first four periods of the Periodic Table using

(a) the electrons-in-boxes method,

(b) *s*, *p*, *d*, *f* notation;

(36) identify an element given values of successive ionization energies;

(37) & (38) plot a graph of first ionization energy against atomic number and use it to explain the term 'periodic';

(39) explain the changes in first ionization energy that take place across the second period;

(40) describe the difference between a continuous spectrum and a line emission spectrum;

(41) explain the emission of light by atoms in terms of excited states;

(42) to (46) state the relationship between

(i) wavelength and frequency,

(ii) energy and frequency (Planck's relationship) and use them in calculations;

(47) & (49) describe the emission spectrum of atomic hydrogen and explain how it is produced;

(48) & (50) sketch at least one series of lines from the hydrogen spectrum and explain what is meant by its convergence limit;

(51) calculate a value for the ionization energy of hydrogen by obtaining the convergence limit graphically.

Check that you have adequate notes before going on to the End-of-Unit Test.

END-OF-UNIT TEST

To find out how well you have learned the material in this Unit, try the test which follows. Read the notes below before starting.

1. You should spend about 1½ hours on this test.
2. You will need a sheet of graph paper.
3. Hand your answers to your teacher for marking.

END-OF-UNIT TEST

Questions 1-3 concern the first six ionization energies for the elements A to E below:

	1st	2nd	3rd	4th	5th	6th	ionization energy (kJ mol^{-1})
A	1090	2350	4610	6220	37 800	47 000	
B	1400	2860	4590	7480	9400	53 200	
C	494	4560	6940	9540	13 400	16 600	
D	736	1450	7740	10 500	13 600	18 000	
E	1310	3390	5320	7450	11 000	13 300	

Select from A to E, the element which is most likely to

1. be in Group IV of the Periodic Table (1)
2. form a chloride of the type MCl_2 (1)
3. form a compound of the type Na_2M (1)

A

In questions 4 to 6 inclusive, one, more than one or none of the suggested responses may be correct. Answer as follows:

A if only 1, 2 and 3 are correct

B if only 1 and 3 are correct

C if only 2 and 4 are correct

D if only 4 is correct

E if some other response, or combination, is correct.

4. From which of the following, TAKEN TOGETHER, can the ionization energy of hydrogen (in kJ mol^{-1}) be calculated?

   A

   1. The value of Planck's constant (in kJ mol^{-1} s).
   2. The value of the Avogadro constant.
   3. The frequency of the limit of convergence of the lines in the ultra-violet emission spectrum of hydrogen (in s^{-1}).
   4. The number of energy levels in the hydrogen atom. (1)

5. The plot below shows the values of the logarithms of the first five ionization energies [lg(I.E.)] of an element *X*.

A

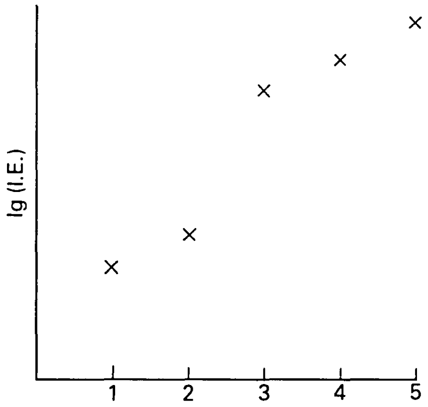


Fig. 41.

This plot shows

1. part of the evidence for the arrangement of the electrons of an atom in energy levels or 'shells'
2. that *X* cannot have an atomic number less than 12
3. that *X* could be an element in Group 2 (an alkaline earth metal)
4. the rise in ionization energy with increasing average distance of the electron from the nucleus (1)

6. Consider the following changes:

A

I $M(s) \rightarrow M(g)$

II $M(s) \rightarrow M^{2+}(g) + 2e^-$

III $M(g) \rightarrow M^+(g) + e^-$

IV $M^+(g) \rightarrow M^{2+}(g) + e^-$

V $M(g) \rightarrow M^{2+}(g) + 2e^-$

The second ionization energy of M could be calculated from the energy values associated with

1. I + V
2. V - III
3. III + IV
4. II - I - III (1)

Questions 7 and 8 are followed by five suggested answers. Select the best answer in each case.

7. The first ionization energy for carbon is greater than it is for sodium. One of the factors responsible is that the

A

A nuclear charge on carbon is greater

B outer quantum shell is further from the nucleus in carbon atoms than in sodium atoms

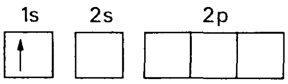
C number of electrons in the outer quantum shell of carbon is greater than in sodium

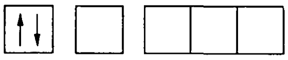
D shielding provided by the inner quantum shells in sodium is greater

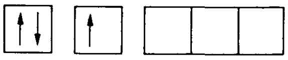
E interatomic bonding in graphite and diamond is stronger than in metallic sodium. (1)

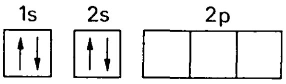
8. The ground-state electronic configurations of five elements are shown below. For which element would you expect the value of the first ionization energy to be the greatest?

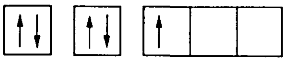
A

A


B


C


D


E


(1)

For questions 9 and 10, choose an answer from A to E as follows:

A Both statements true: second explains first

B Both statements true: second does not explain first

C First true: second false

D First false: second true

E Both false

	First statement	Second statement		
9.	Gaseous elements, excited by a high-voltage electrical discharge, emit light of characteristic colours.	When gaseous elements are excited by a high voltage electric discharge, only energies equal to the characteristic ionization energies of the different elements are being radiated.	A	(1)
10.	The first ionization energies of elements decrease down a group of the Periodic Table.	In descending a group of the Periodic Table, the shielding effect of inner electron shells increases and the outermost electron shell becomes further from the nucleus.	A	(1)

11. The first seven types of orbitals permitted for any atom are, in random order, $2s$, $3p$, $4s$, $3d$, $1s$, $2p$, $3s$.

A part

If the atom is Ca, write down the orbitals in order of increasing energy (from left to right) and give the number of electrons in each orbital. (2)

12. (a) Sketch a line spectrum of hydrogen (Lyman series only, wavelength increasing from left to right). (2)

A part

(b) The charge on the oxygen nucleus is eight times that on the hydrogen nucleus and yet the first ionization energies of hydrogen and oxygen are almost identical (1300 kJ mol^{-1}). Suggest reasons for this (2)

A

13. In the table below, the first, second and third ionization energies of six successive elements in the Periodic Table are listed. The elements have been arbitrarily denoted by the letters A to F. All energy values are given in kJ mol^{-1}.

Table 11

	A	B	C	D	E	F
1st Ionization Energy	1013	1000	1255	1519	418	590
2nd Ionization Energy	1904	2255	2297	2665	3067	1146
3rd Ionization Energy	2916	3389	3853	3933	4393	4916

(a) (i) Which one of the elements A to F is likely to be a noble gas?
(ii) Give reason(s) for your answer. (2)

(b) In the light of your answer to (a), suggest the names of a set of chemical elements that could be represented by A to F. (2)

(c) State the equation representing the processes to which the ionization energies refer. Use the symbol Z to denote the element. (3)

(d) The first ionization energy of some elements may be determined by an 'electron impact' method. The following is a schematic diagram of the apparatus used for this.

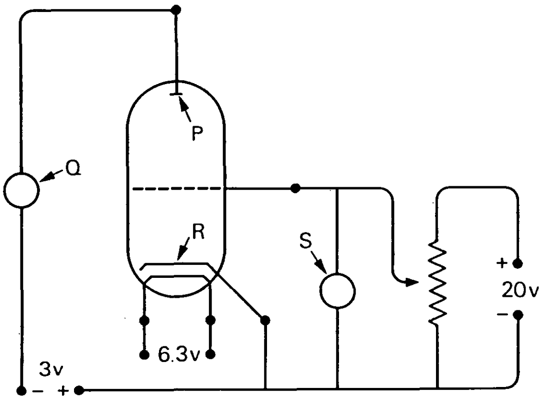


Fig. 42.

(i) Label the parts of the apparatus marked by letters P to S in the diagram.

(ii) What materials, if any, apart from the electrodes should be contained inside the tube? (1)

(iii) Sketch a graph showing the approximate experimental results which would be obtained with the apparatus. (Good labelling is important.) (3)

14.

A

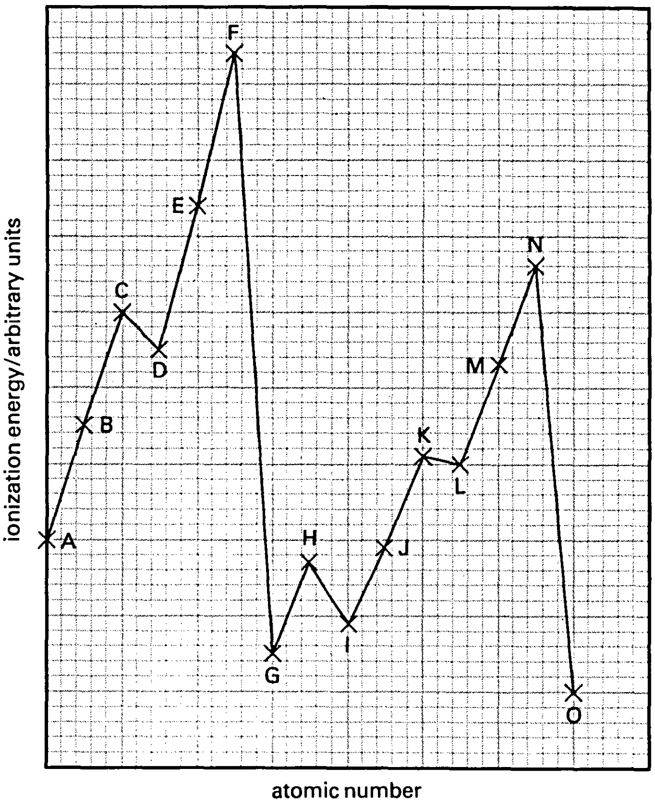


Fig. 43.

The graph shows the first ionization energies of fifteen successive elements in the Periodic Table, lettered A to O, all with atomic numbers less than 25.

(a) Using the letters A to O as appropriate (and not the chemical symbols which you know or think these letters represent) select:

(i) two alkali metals (Group 1 metals);

(ii) an element which forms no true chemical compounds. (2)

(b) Although the graph shows an overall rise in first ionization energy from element G to element N, the value for element I is lower than for element H. How may this be explained? (2)

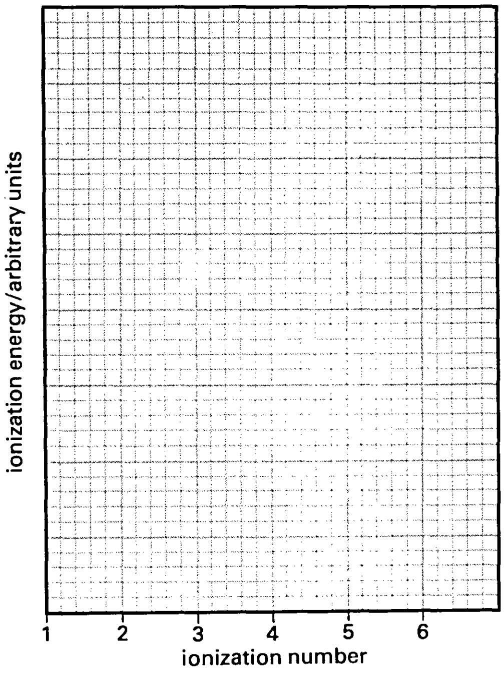


Fig. 44.

(c) On graph paper, sketch the graph showing the first six successive ionization energies of the element G. (2)

(d) All the elements A to O have some electrons in *s*-orbitals. Describe, by a diagram or otherwise, the distribution of electron density round the nucleus for an *s*-orbital. (2)

(e) Which of the elements A to O are in the *s*-block and which in the *p*-block? (2)

15. (a) An isotope of uranium is represented by the symbol ${}^{234}_{92}U$. What is the significance of the two numbers?

(b) Identify A, B, C, D and E in the following equations:

(i) ${}^{234}_{92}U \rightarrow \alpha + A$

(ii) ${}^{239}_{92}U \rightarrow \beta + B$

(iii) ${}^{235}_{92}U \rightarrow \gamma + C$

(iv) ${}^{238}_{92} + {}^{2}_{1}H \rightarrow {}^{239}_{92}U + D$

(v) ${}^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{95}_{42}Mo + {}^{139}_{57}La + 2{}^{1}_{0}n + 7E$ (6)

(c) In the reaction represented by equation (v), the product particles have approximately 0.1% less mass than the reactant particles. What is the significance of this? (2)

16. Here is some information concerning element X, of atomic number 31. In its natural state, it consists of a mixture of two isotopes X_A and X_B.

Table 12

Isotope	Isotopic mass	Percentage abundance
X_A	69.0	60.2
X_B	71.0	39.8

Its first four ionization energies are 580, 2000, 3000 and 6200 kJ mol^{-1}.

(a) Calculate a value for the relative atomic mass of X correct to three significant figures. (3)

(b) (i) Write down the electronic configuration (in terms of *s*,*p* and *d* levels) of element X in its ground state.

(ii) In which group of the Periodic Table is X placed? (2)

(c) Explain why:

(i) The difference between the first and second ionization energies is greater than that between the second and third ionization energies. (2)

(ii) The difference between the third and fourth ionization energies is much larger than that between the other successive energies. (2)

(Total 60 marks)

APPENDIX ONE

A HISTORICAL PERSPECTIVE

So far in this Unit we have not included a historical account of the work which led to the models of atomic structure we have outlined. This is partly because you can understand something without knowing the details of its historical development and partly because few examination boards require such knowledge.

However, we hope you will be interested to read about some of the work that was done - particularly since the turn of the century - and consider its implications for society today. In this appendix, we give some outline notes and suggestions for further reading. However, our list is not exhaustive and new books are appearing all the time so you should see what is available in your school or local library.

Check with your teacher whether your examination board does require any historical knowledge. As a guide, we include some typical examination questions in this subject area which you should try, if appropriate.

Chronological table of some important developments in atomic theory

1803 - Dalton's theory of identical atoms

1884 - Balmer observed the visible spectrum of hydrogen

1896 - Becquerel discovered radioactivity

1897 - Thomson discovered the electron

1911 - Rutherford proposed the nuclear atom

1913 - Moseley defined atomic number; Rutherford and Soddy discovered isotopes; Bohr's theory of planetary electrons in atoms

1919 - Rutherford transmuted ^{14}N to ^{17}O by α-bombardment

1932 - Chadwick characterised neutrons in beam from Be by α-bombardment

1939 - Hahn and Strassmann discovered atomic fission

1945 - Hiroshima and Nagasaki destroyed by fission bombs

1952 - Nuclear fusion bomb (hydrogen bomb) at Bikini Atoll

1956 - First nuclear fission power-station, Calder Hall, Cumbria

1960's - Attempts to harness nuclear fusion (Sakharov and others)

1970's - The hunting of the (alleged) quark

Some of the many books which you may find useful are listed below:

Atomic structure

Asimov, Isaac: Understanding physics; the electron, proton and neutron. (Signet, 1966)

Gowing, Margaret: *Reflections on atomic energy history.* (Rede Lecture, 1978).
0521 22392 X

Jones, Rotblat & Whitrow: *Atoms and the universe.* (Pelican, 1973).
0140 215514

Oliver, H.P.H.: *Inside the atom* - Nuffield Chemistry background book.
(Longman, 1971) 0140 82330 1

Stableford, Brian: *The mysteries of modern science* - Chapter 2
(Routledge & Kegan Paul, 1977) 07100 86970

Nuclear energy

Bacon, Hilary & Valentine, John: *Power corrupts.* (Pluto Press, 1981).
0 8610 43456

Croall, Stephen & Sempler, Kaianders: *Nuclear power for beginners.*
(Beginners Books Ltd., Writers and readers Co-op., 1981) 0 906386 063

Patterson, Walter: *Nuclear power.* (Penguin, 1976). 0 1402 1930 7

Dalton's atomic theory

Dalton was not the first to propose that matter was particulate rather than continuous. The Greek philosopher, Democritus, in 400 BC, suggested that there were unsplittable particles which we now call atoms (from the Greek a = not, tomos = I cut) and in the 17th century Isaac Newton said "It seems probable to me that God in the beginning formed matter in solid, massy, hard, impenetrable, moveable particles, of such sizes, and figures, and with such other properties, and in such proportion, as most conduced to the end for which He formed them".

However, Dalton was the first to base an atomic theory on experiment. At the birth of modern chemistry in the late 18th century, when many new elements were being discovered by Priestley, Scheele, Davy and others, John Dalton (working in Manchester) identified the "Laws of Chemical Combination by Weight". These included the law of conservation of matter, the law of constant composition and the law of multiple proportions; and they could be explained by his atomic theory.

For further information on these laws, you should consult older textbooks. You may also be interested in trying experiments to illustrate the laws, in which case you should consult your teacher.

Dalton's theory had its weaknesses. He thought water was HO, he did not know about isotopes and he did not foresee the "splitting of the atom" by 20th century nuclear physicists.

Look at the propositions of Dalton's atomic theory and suggest how each one might be modified in the light of modern knowledge. Bear in mind, however, that his simple 'model' of matter is still quite useful both as a first introduction to the subject and also in topics where a more sophisticated model is not necessary. An example of the latter is the kinetic theory of gases which you will study in a later Unit.

The discovery of the electron

Read about the work of Crookes and J.J. Thomson on 'cathode rays' which they observed when an electrical discharge was passed through a gas at low pressure. The properties of these rays showed them to consist of particles, each very much smaller than an atom and with a negative charge.

The Geiger-Marsden experiment

Geiger and Marsden, working under the direction of Lord Rutherford, employed a stream of α-particles from a radioactive source for bombarding a thin sheet of gold or other metal. They found that most of the particles went straight through, but that a small fraction rebounded, as shown in Fig. 45.

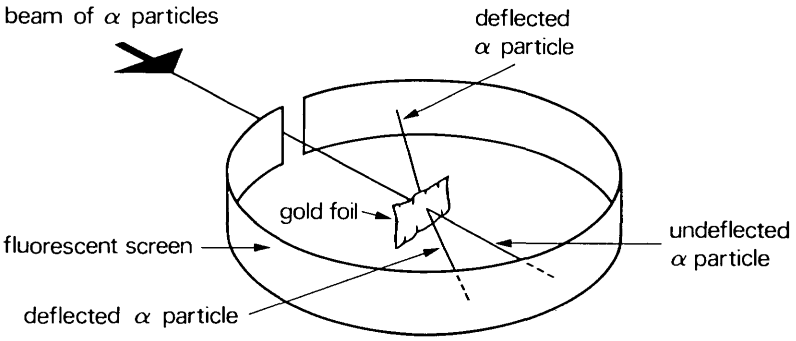


Fig. 45. The Geiger-Marsden experiment

Read about this experiment to understand how it showed that the material in gold atoms is concentrated in compact nuclei, like stones in plums. Rutherford suggested the nuclei were positively charged and the outer regions contained electrons of compensating negative charge and, as you have already learned, this model was further elaborated by Bohr and others.

Moseley's experiment

In 1913, Moseley showed that there were no gaps in the first forty or so elements in the Periodic Table. He obtained X-rays from each element in turn and found their frequencies by diffracting them, using a crystal of potassium hexacyanoferrate(III) (also known as potassium ferricyanide), as shown in Fig. 46.

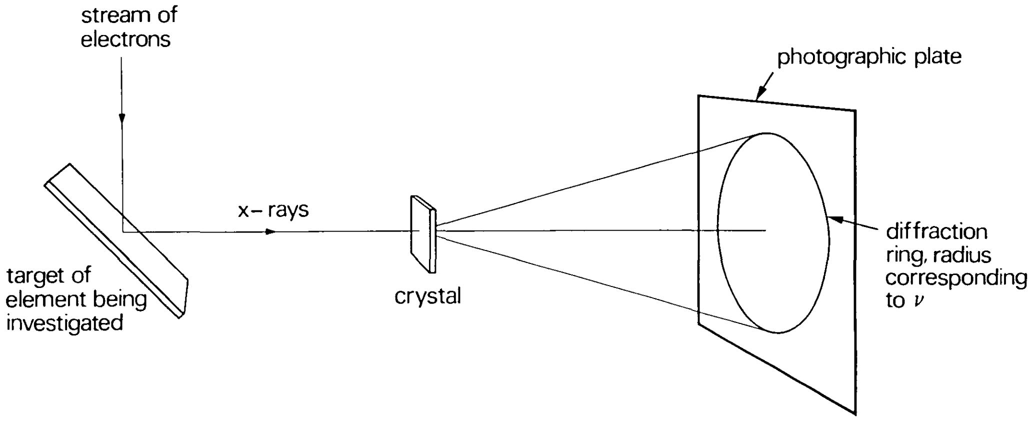


Fig. 46. Moseley's experiment

Find out how the variation of the frequency of the X-rays with the identity of the element showed that atomic number Z is a fundamental characteristic of an element and not just the position of that element in a list. Also, look for the reasoning which showed that there were no gaps in the first forty or so elements in the Periodic Table.

Together with the discovery of isotopes at about the same time, Moseley's work led to the search for the neutron which, however, was not finally identified for nearly twenty years.

Consolidation

To consolidate your reading, you should now attempt the following teacher-marked exercise, which consists of parts of three A-level questions. This exercise is designed to help you organise your ideas about certain aspects of the history of atomic structure. Before you start writing, read through any notes you have made and check over any points you are not sure about in a suitable book. Then put away your notes and allow about 45 minutes to write an answer.

Teacher-marked Exercise

(a) Summarise the observations which led to the discovery of the electron. On what experimental evidence is the electron regarded as being both particle-like and wave-like in nature?

(b) For each of the following classical experiments, describe briefly what was done, what was observed, and what was deduced.

(i) Geiger and Marsden's experiment;

(ii) Moseley's experiment.

(c) Describe in outline how a beam of neutrons can be produced. State briefly what experimental evidence led to the conclusion that a neutron has

(i) no electric charge;

(ii) a mass approximately equal to that of the proton.

APPENDIX TWO

The relationship between charge and energy

In Experiment 1, you used a conversion factor to obtain a value for the energy acquired by electrons when accelerated by a measured voltage. We now derive this conversion factor.

It follows from basic definitions that one coulomb (1 C) of charge accelerated by a potential difference of one volt (1 V) gains one joule (1 J) of energy, i.e. 1 C accelerated by 1 V gains 1 J.

The charge on an electron is 1.6×10^{-19} C

$\therefore$ 1 electron accelerated by 1 volt gains 1.6×10^{-19} J

There are 6.02×10^{23} electrons in 1 mol of electrons

$\therefore$ 1 mol of electrons accelerated by 1 V gains $1.6 \times 10^{-19} \times 6.02 \times 10^{23}$ J
$= 96300$ J

The energy acquired by a single electron accelerated by one volt is sometimes referred to as one electron-volt (ev), and ionization energies are sometimes quoted in electron-volts. The calculation above shows that:

$$\boxed{1 \text{ eV} \equiv 96.3 \text{ kJ mol}^{-1}}$$

APPENDIX THREE

ADDITIONAL EXERCISES

You can use the exercises in this Appendix to give you extra practice in some of the types of calculation you have already met in the Unit. They may also be useful for revision.

Calculating relative atomic mass from percentage abundance

Exercise 71 Chlorine consists of isotopes of relative masses 34.97 and 36.96 with natural abundances of 75.77% and 24.23% respectively.

Calculate the mean relative atomic mass of naturally-occurring chlorine.

Exercise 72 Calculate the relative atomic mass of natural lithium which consists of 7.4% of ^{6}Li (relative atomic mass 6.02) and 92.6% of ^{7}Li (relative atomic mass 7.02).

Exercise 73 Copper (atomic number 29) has two isotopes, the first of relative atomic mass 62.9 and abundance 65%, the second of relative atomic mass 64.9 and abundance 35%.

Calculate the mean relative atomic mass of naturally-occurring copper.

Exercise 74 Using mass spectrometry, the element gallium has been found to consist of 60.4 per cent of an isotope of atomic mass 68.93 and 39.6 per cent of an isotope of atomic mass 70.92.

Calculate, to three significant figures, the relative atomic mass of gallium.

Answers to all the exercises in this section are on page 96.

ANSWERS

(Answers to questions from examination papers are provided by ILPAC and not by the Examination Boards).

Exercise 1

The scale factor is given by:

$$\frac{\text{diameter of earth}}{\text{diameter of football}} = \frac{13000 \times 10^3\ \text{m}}{22 \times 10^{-2}\ \text{m}} = 5.9 \times 10^7$$

∴ the diameter of an atom would become $5.9 \times 10^7 \times 0.32$ nm

$= 1.9 \times 10^7$ nm $= 1.9$ cm

This is the diameter of a 1p piece. Correct answer = $\boxed{\text{B}}$

Exercise 2

$$\frac{\text{radius of atom}}{\text{radius of nucleus}} = \frac{10^{-10}\ \text{m}}{10^{-15}\ \text{m}} = 10^5$$

∴ if the nucleus were 1 mm in diameter, the atom would be 1×10^5 mm in diameter or $\boxed{100\ \text{m}}$

This is approximately the length of a football pitch.

Exercise 3

(a) First the mass of the nucleus is calculated by substituting into the expression:

$$m = \frac{M}{L}$$

where $M = 23.0\ \text{g mol}^{-1}$, $L = 6.02 \times 10^{23}\ \text{mol}^{-1}$

This gives: $m = \dfrac{23.0\ \text{g mol}^{-1}}{6.02 \times 10^{23}\ \text{mol}^{-1}} = 3.82 \times 10^{-23}$ g

Substituting into the expression:

$$\text{density} = \frac{m}{V_N}$$

where $m = (3.82 \times 10^{-23} / 1000)$ kg $= 3.82 \times 10^{-26}$ kg

and $V_N = 1.73 \times 23.0 \times 10^{-45}\ \text{m}^3 = 3.98 \times 10^{-44}\ \text{m}^3$

gives density $= \dfrac{3.82 \times 10^{-26}\ \text{kg}}{3.98 \times 10^{-44}\ \text{m}^3} = \boxed{9.60 \times 10^{17}\ \text{kg m}^{-3}}$

(b) See next page.

Exercise 3 (cont.)

(b) This involves an extra step at the end to express mass in ton and volume in mm^3.

From your data book:

$1\ \text{ton} = 1.016 \times 10^3$ kg

∴ $1\ \text{kg} = \dfrac{1\ \text{ton}}{1.016 \times 10^3}$

∴ $m = 3.82 \times 10^{-26}\ \text{kg} = \dfrac{3.82 \times 10^{-26}}{1.016 \times 10^3}\ \text{ton} = 3.76 \times 10^{-29}$ ton

Also, $1\ \text{m}^3 = 10^9\ \text{mm}^3$

∴ $V_N = 3.98 \times 10^{-44}\ \text{m}^3 = 3.98 \times 10^{-44} \times 10^9\ \text{mm}^3 = 3.98 \times 10^{-35}\ \text{mm}^3$

∴ density $= \dfrac{m}{V_N} = \dfrac{3.76 \times 10^{-29}\ \text{ton}}{3.98 \times 10^{-35}\ \text{mm}^3} = \boxed{9.45 \times 10^5\ \text{ton mm}^3}$

Do you realise that a nucleus the size of a pinhead (1 mm^3) would weigh 9.45×10^5 ton - almost a million tons?!

Exercise 4

(a) Radius of Na atom = 0.186 nm $= 0.186 \times 10^{-9}$ m

∴ volume of Na atom $= \frac{4}{3}\pi r^3 = \frac{4}{3} \times 3.142 \times (0.186 \times 10^{-9}\ \text{m})^3$

$= \boxed{2.70 \times 10^{-29}\ \text{m}^3}$

(b) Fraction $= \dfrac{V\ (\text{nucleus})}{V\ (\text{atom})} = \dfrac{3.98 \times 10^{-44}\ \text{m}^3}{2.70 \times 10^{-29}\ \text{m}^3} = \boxed{1.47 \times 10^{-15} \text{ or } \dfrac{1}{6.78 \times 10^{14}}}$

Exercise 5

The atomic number of an atom is the number of protons in its nucleus.

The mass number of an atom is the total number of protons and neutrons in its nucleus. (Protons and neutrons are known collectively as nucleons.)

Exercise 6

Isotopes are atoms of the same element with different numbers of neutrons; e.g. nitrogen has two stable isotopes, one containing 7 protons and 7 neutrons, the other 7 protons and 8 neutrons.

Exercise 7

(a) W - 18; X - 19; Y - 19; Z - 18.

In each case, the number of neutrons is substracted from the mass number.

(b) Isotopes: W and Z
X and Y

Exercise 8

(a) (i) $^{36}_{18}Ar$; $^{38}_{18}Ar$; $^{40}_{18}Ar$.

(ii) $^{63}_{29}Cu$; $^{65}_{29}Cu$.

(iii) $^{28}_{14}Si$; $^{29}_{14}Si$; $^{30}_{14}Si$.

(b) $^{36}_{18}Ar$ - 18; $^{38}_{18}Ar$ - 20; $^{40}_{18}Ar$ - 22.

$^{63}_{29}Cu$ - 34; $^{65}_{29}Cu$ - 36.

$^{28}_{14}Si$ - 14; $^{29}_{14}Si$ - 15; $^{30}_{14}Si$ - 16.

In each case, the subscript (atomic number) is subtracted from the superscript (mass number).

Exercise 9

(b) A vaporised sample D connection to vacuum pump
B electron source E magnetic field
C electric field F detector for positive ions

(c) Vaporised sample. Atoms must be in the gaseous state before they can be ionised.

Electron source. A stream of electrons is used to bombard the atoms of the vaporised sample and strip electrons off them, forming positive ions. The main process that takes place is, for an element X:

$$X(g) \rightarrow X^+(g) + e^-$$

The source is usually a tungsten filament which gives off electrons when a current is passed through it.

Electric field. An electrode with a negative potential attracts the positive ions and accelerates them as they move towards it.

The electrode contains a pair of slits which further restricts the stream of ions to a very narrow beam.

Connection to a vacuum pump. The whole apparatus is evacuated at the start of the experiment. This allows the positive ions to travel in straight lines without collision.

Magnetic field. A powerful magnet sets up a magnetic field which deflects the positive ions in the beam. The extent of deflection depends on the mass and charge of the ion.

By altering the strength of the magnetic field, ions of different mass-to-charge ratio can be brought into focus on the detector.

Detector. This is an electronic measuring device. The signal from the positive ions is amplified and recorded by a pen recorder giving a series of peaks corresponding to the different ions produced from the sample. In a mass spectrograph, the ions strike a photographic plate, producing a series of lines called a mass spectrum. In both cases, samples of known standards are also run and the unknowns worked out by comparison.

Exercise 10

(a) (i) $^{222}_{86}Rn^+$; $^{220}_{86}Rn^+$

(ii) $^{220}_{86}Rn^+$

Lighter isotopes are deflected more in a given magnetic field.

(b) (i) Increase the strength of the magnetic field. This increases the deflection of the ions and would draw those at Y towards the detector.

(ii) Decrease the strength of the electric field, by decreasing the voltage between the accelerator plates. This decreases the momentum of the ions and therefore increases their deflection in the magnetic field.

(c) Rn^{2+} ions would be deflected more than the ions at X and Y. For a given electric and magnetic field strength, the deflection of the ions depends on their mass-to-charge ratio. The smaller the ratio, the greater is the deflection.

Exercise 11

(a) $^{87}_{37}Rb$; $^{85}_{37}Rb$

(b) The height of each peak is proportional to the relative abundance of the isotope it represents. In this case, $^{85}_{37}Rb$ is more than twice as abundant as $^{87}_{37}Rb$.

Exercise 12

(a) Height of lithium-6 peak = 0.50 cm

Height of lithium-7 peak = 6.30 cm

Substituting into the expression:

$$\% \text{ abundance} = \frac{\text{amount of isotope}}{\text{total amount of all isotopes}} \times 100$$

$$\% \text{ abundance of } ^6Li = \frac{0.50}{6.30 + 0.50} \times 100 = \boxed{7.4\%}$$

$$\% \text{ abundance of } ^7Li = \frac{6.30}{6.30 + 0.50} \times 100 = \boxed{92.6\%}$$

(b) Total mass of a hundred atoms = (6 x 7.4) + (7 x 92.6) amu
= 44.4 + 648.2 amu = 692.6 amu
= 693 amu (3 significant figures)

substituting into the expression:

$$\text{Average mass} = \frac{\text{total mass}}{\text{number of atoms}}$$

$$\text{Average mass} = \frac{693}{100} \text{ amu} = 6.93 \text{ amu}$$

$$\therefore \text{ relative atomic mass} = \boxed{6.93}$$

Exercise 13

The mass/charge ratios refer to the singly-charged ions from the isotopes present in the sample: ${}^{20}_{10}Ne$; ${}^{21}_{10}Ne$; ${}^{22}_{10}Ne$

The relative intensities show the relative abundance of each isotope in the sample.

Substituting into the expression:

$$\% \text{ abundance} = \frac{\text{amount of isotope}}{\text{total amount of all isotopes}} \times 100$$

$$\% \text{ abundance of } {}^{20}Ne = \frac{0.910}{0.910 + 0.0026 + 0.088} \times 100 = 91\%$$

$$\% \text{ abundance of } {}^{21}Ne = \frac{0.0026}{0.910 + 0.0026 + 0.088} \times 100 = 0.26\%$$

$$\% \text{ abundance of } {}^{22}Ne = \frac{0.088}{0.910 + 0.0026 + 0.088} \times 100 = 8.8\%$$

(Did you notice that the sum of the relative intensities is 1?)

$$\text{Total mass of 100 atoms} = (20 \times 91) + (21 \times 0.26) + (22 \times 8.8)$$
$$= 1820 + 5.46 + 193.6 = 2.02 \times 10^3 \text{ amu}$$

$$\text{Average mass} = \frac{\text{total mass}}{\text{number of atoms}} = \frac{2.02 \times 10^3 \text{ amu}}{100} = 20.2 \text{ amu}$$

$\therefore$ relative atomic mass = $\boxed{20.2}$

Exercise 14

(a) ${}^{50}_{24}Cr$ - 4.31%; ${}^{52}_{24}Cr$ - 83.76%; ${}^{53}_{24}Cr$ - 9.55%; ${}^{54}_{24}Cr$ - 2.38%

(b)

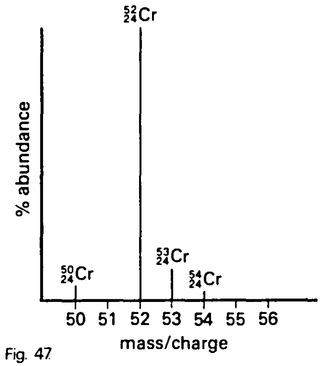


Fig. 47

Total mass of 100 atoms

$= (50 \times 4.31) + (52 \times 83.76)$

$\quad + (53 \times 9.55) + (54 \times 2.38)$

$= 215.5 + 4355.2 + 506.15 + 128.52$

$= 5.21 \times 10^3$ amu

$\therefore$ average mass $= \frac{5.21 \times 10^3 \text{ amu}}{100}$

$= 52.1$ amu

and relative atomic mass = $\boxed{52.1}$

Exercise 15

(a) (i) The positions of Te and I would be reversed.

(ii) The positions of Ar and K would be reversed.

(b) There is only one stable isotope of iodine - ${}^{127}_{53}I$. The relative atomic mass is therefore 127. Tellurium has no fewer than eight stable isotopes, but the most abundant are ${}^{128}_{52}Te$ and ${}^{130}_{52}Te$, each of which has more neutrons than ${}^{127}_{53}I$, but fewer protons. Thus, the relative atomic mass of tellurium is greater than that of iodine, even though the atomic number is smaller. In the same way, heavy isotopes of argon, mainly ${}^{40}_{18}Ar$, give it a greater relative atomic mass than potassium, which consists mainly of ${}^{39}_{19}K$.

Exercise 16

Mass/charge ratio	Species
35	${}^{35}_{17}Cl^+$
37	${}^{37}_{17}Cl^+$
70	$({}^{35}_{17}Cl—{}^{35}_{17}Cl)^+$
72	$({}^{35}_{17}Cl—{}^{37}_{17}Cl)^+$
74	$({}^{37}_{17}Cl—{}^{37}_{17}Cl)^+$

Exercise 17

${}^{4}_{2}He$ atom contains 2 protons, 2 neutrons and 2 electrons

$$\therefore \text{ relative atomic mass} = (2 \times 1.007276) + (2 \times 1.008665) + (2 \times 0.000548)$$
$$= 2.014552 + 2.017330 + 0.001096 = \boxed{4.032978}$$

i.e. the He atom is less massive than its parts by 0.030380 amu or 0.76%

Exercise 18

(a) 1 amu = 1.66×10^{-27} kg

$\therefore$ mass defect = $0.030380 \times 1.66 \times 10^{-27}$ kg = 5.04×10^{-29} kg

Since there are 6.02×10^{23} atoms in one mole of He,
mass defect for one mole = 5.04×10^{-29} kg $\times 6.02 \times 10^{23}$

$= 3.03 \times 10^{-5}$ kg (0.03 g)

Substituting the mass into the equation:

$$E = mc^2$$

where $c = 2.99 \times 10^8$ m s^{-1}

gives $E = 3.03 \times 10^{-5}$ kg $\times (2.99 \times 10^8 \text{ m s}^{-1})^2 = 2.71 \times 10^{12}$ kg m^2 s^{-2}

But 1 kg m^2 s^{-2} = 1 J

$\therefore$ binding energy = 2.71×10^{12} J or $\boxed{2.71 \times 10^9 \text{ kJ}}$

(b) Percentage $= \frac{331 \text{ kJ}}{2.71 \times 10^9 \text{ kJ}} \times 100 = \boxed{1.22 \times 10^{-5}\%}$

(i.e. the contribution of the electrons to the binding energy and mass defect is negligible.)

Exercise 19

(a) P - α-particles ($^{4}_{2}He$); Q - γ rays; R - β-particles ($^{0}_{-1}e$)

(b) A magnetic field, operating in a direction perpendicular to the plane of the paper would cause a similar pattern of deflection.

Exercise 20

Table 3

Emission	Nature	Relative mass and charge		Symbol	Extent of deflection in electric or magnetic field	Relative penetration
alpha, α	helium nuclei	4	+2	$^{4}_{2}He$	small	1
beta, β	electrons	$\frac{1}{1840}$	-1	$^{0}_{-1}e$	large	100
gamma, γ	electro-magnetic radiation	none	none	none	none	10000

Exercise 21

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

Exercise 23

(a) $^{212}_{84}Po \rightarrow {}^{0}_{-1}e + {}^{212}_{85}At$

(b) $^{24}_{11}Na \rightarrow {}^{0}_{-1}e + {}^{24}_{12}Mg$

(c) $^{108}_{47}Ag \rightarrow {}^{0}_{-1}e + {}^{108}_{48}Cd$

Exercise 22

(a) $^{212}_{84}Po \rightarrow {}^{4}_{2}He + {}^{208}_{82}Pb$

(b) $^{220}_{86}Rn \rightarrow {}^{4}_{2}He + {}^{216}_{84}Po$

Exercise 24

(a) $^{226}_{88}Ra \rightarrow {}^{4}_{2}He + {}^{222}_{86}Rn$

(b) $^{43}_{19}K \rightarrow {}^{0}_{-1}e + {}^{43}_{20}Ca$

(c) $^{43}_{20}Ca \rightarrow {}^{4}_{2}He + {}^{39}_{18}Ar$

Exercise 25

(a) For α-emission, the atomic number decreases by two and the mass number decreases by four.

(b) For β-emission, the atomic number increases by one and the mass number remains the same.

Exercise 26

(a) $^{209}_{83}Bi$

Note that all nuclei with $Z < 83$ are unstable, regardless of the neutron to proton ratio.

(b) (i) $N/Z = \frac{209-83}{83} = \frac{126}{83} = \boxed{1.52}$

(ii) $N/Z = \frac{108-48}{48} = \frac{60}{48} = \boxed{1.15}$

(iii) $N/Z = \frac{12-6}{6} = \frac{6}{6} = \boxed{1.00}$

(c) The neutron to proton ratio for stable nuclei increases steadily from about 1.0 for the lightest nuclei to about 1.5 for the heaviest nuclei.

(d) (i) $^{11}_{6}C$ $N/Z = \frac{5}{6} < 1$ This is too low for stability. The graph confirms that $^{11}_{6}C$ is unstable.

(ii) $^{60}_{30}Zn$ $N/Z = \frac{30}{30} = 1.00$ This is too low for stability. The graph confirms that $^{60}_{30}Zn$ is unstable.

(iii) $^{106}_{47}Ag$ $N/Z = \frac{59}{47} = 1.26$ This is about right for stability. However, the graph does not show $^{106}_{47}Ag$ because it is, in fact, unstable.

Note that a favourable N/Z ratio does not guarantee stability.

(iv) $^{143}_{56}Ba$ $N/Z = \frac{87}{56} = 1.55$ This is too high for stability. The graph confirms that $^{143}_{56}Ba$ is unstable.

(v) $^{206}_{82}Pb$ $N/Z = \frac{124}{82} = 1.51$ This is about right for stability. The graph confirms that $^{206}_{82}Pb$ is stable.

Exercise 27

(a) $^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}e$

(b) Reactant: $N/Z = \frac{14-6}{6} = \boxed{1.33}$

Product: $N/Z = \frac{14-7}{7} = \boxed{1.00}$

(c) The N/Z ratio for the reactant is too high for a light stable nucleus. The emission of an electron reduces N, the number of neutrons, by one but increases Z, the number of protons, also by one. In this way, β-emission reduces the N/Z ratio to a suitable value for stability.

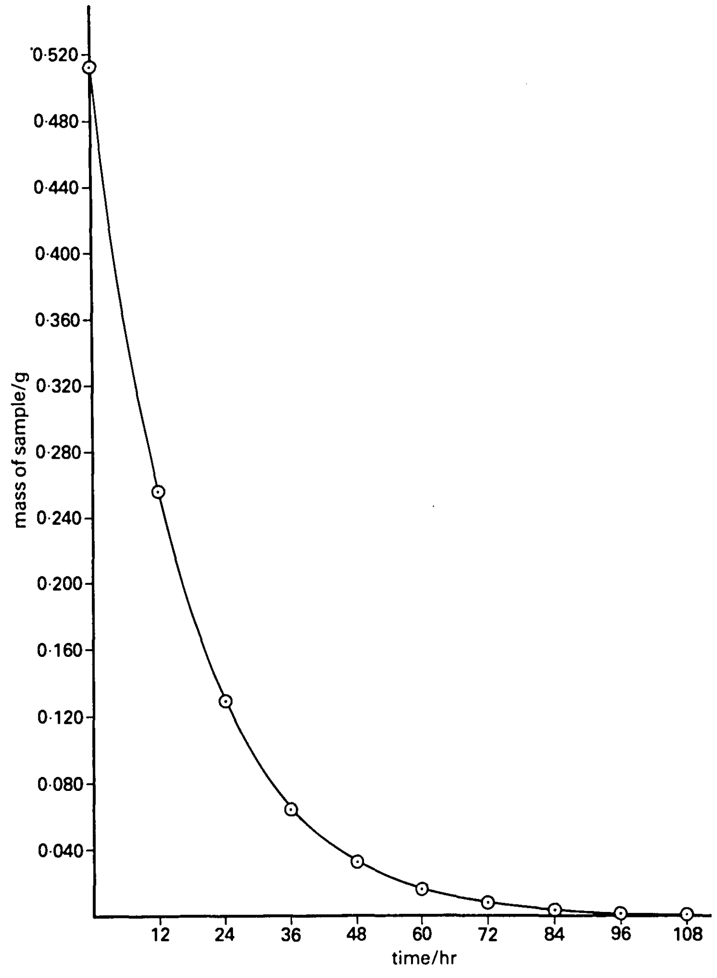
Exercise 28

(a) The half-life of a radioactive isotope is the time taken for a given amount of isotope to decay to half the original amount.

(b) Since radioactive decay is an exponential process, it carries on to infinity, or at least to levels where the rate is no longer statistically significant. In other words, decay becomes slower and slower but never actually stops. This means that it is impossible to measure the 'total life' of a radioisotope.

Exercise 29

(a) Fig 48.



Exercise 29 (cont.)

(b) The rate decreases as the reaction proceeds. Since the rate of decay is proportional to the amount of isotope remaining at any time, it decreases exponentially as the amount of radioisotope decreases.

(c) Theoretically, the amount would never reach zero, as this is an exponential process.

(d) The shape of the curve would be the same if activity had been plotted because activity is proportional to mass.

(e) There are two ways of answering this questions.

(i) The graph shows the mass of the sample.decreasing by half every twelve hours, i.e. the half life is 12 hours and 10 half lives = 120 hours. Since activity is proportional to mass, the percentage of activity remaining after 10 half lives

$$= \frac{\text{mass after 120 hours}}{\text{original mass}} \times 100$$

$$= \frac{0.0005\ \text{g}}{0.512\ \text{g}} \times 100 = \boxed{0.1\%}$$

(ii) Without reference to the graph, an answer is obtained more precisely: fraction left after 10 half-lives

$$= \tfrac{1}{2} \times \tfrac{1}{2} \times \tfrac{1}{2} \times \tfrac{1}{2} \times \tfrac{1}{2} \times \tfrac{1}{2} \times \tfrac{1}{2} \times \tfrac{1}{2} \times \tfrac{1}{2} \times \tfrac{1}{2}$$

$$= (\tfrac{1}{2})^{10} = 9.77 \times 10^{-4}$$

$$\% = \text{fraction} \times 100 = \boxed{0.0977\%}$$

Exercise 30

(a) $^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}H$

(b) The relative activity of the sample compared with the activity of new wood

$$= \frac{\text{activity of sample}}{\text{activity of new wood}} = \frac{7.5\ \text{counts min}^{-1}\ \text{g}^{-1}}{15.0\ \text{counts min}^{-1}\ \text{g}^{-1}} = 0.50$$

Since the sample has an activity of half that of new wood, one half life has elapsed.

$\therefore$ year in which tomb was built = 1982 AD - 5730 = $\boxed{3748\ \text{BC}}$

The method is not as accurate as this answer implies. It would be safer to say the tomb was built between 3700 BC and 3800 BC.

(c) The amount of carbon-14 in the atmosphere is assumed to be constant so that the % of carbon-14 in freshly-grown wood is also constant.

Exercise 31

$^{239}_{92}U \rightarrow ^{0}_{-1}e + ^{239}_{93}Np$

$^{239}_{93}Np \rightarrow ^{0}_{-1}e + ^{239}_{94}Pu$

Exercise 32

$^{239}_{94}Pu + ^{4}_{2}He \rightarrow ^{242}_{96}Cm + ^{1}_{0}n$

Exercise 33

(a) $^{16}_{9}F + ^{1}_{0}n \rightarrow ^{13}_{7}N + ^{4}_{2}He$

(b) $^{17}_{8}O + ^{4}_{2}He \rightarrow ^{20}_{10}Ne + ^{1}_{0}n$

(c) $^{15}_{7}N + ^{1}_{1}H \rightarrow ^{12}_{6}C + ^{4}_{2}He$

Exercise 34

(a) $^{238}_{92}U + ^{14}_{7}N \rightarrow ^{247}_{99}Es + 5^{1}_{0}n$

(b) $^{246}_{96}Cm + ^{13}_{6}C \rightarrow ^{251}_{102}No + 8^{1}_{0}n$

(c) $^{252}_{98}Cf + ^{10}_{5}B \rightarrow ^{257}_{103}Lw + 5^{1}_{0}n$

Exercise 35

$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{142}_{58}Ba + ^{92}_{34}Se + 2^{1}_{0}n$

Exercise 36

(a) First ionization energy is the energy required to remove each outermost electron from one mole of atoms of an element in its gaseous state.

(b) $Na(g) \rightarrow Na^{+}(g) + e^{-}$

(c) First ionization energy of sodium = 500 kJ mol^{-1}

Experiment 1

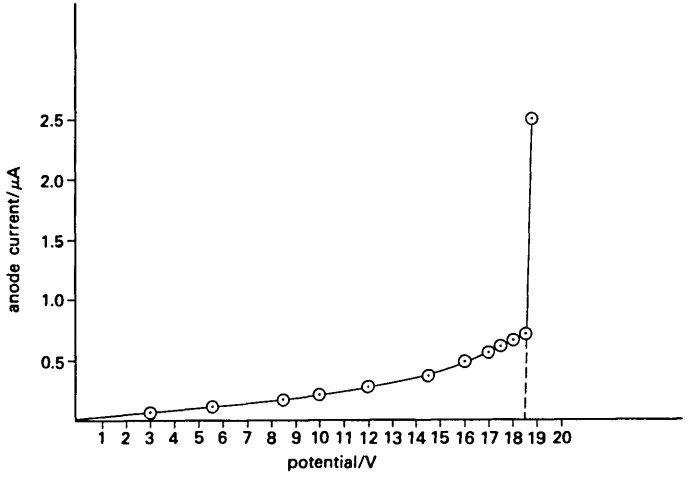
Answer to Question 1

(a) A current flows between the grid and the cathode before ionization because the electrons repelled by the negative valve anode return to the grid and then flow round the circuit.

(b) Every argon atom which ionizes produces an extra electron which returns to the grid. This causes a sudden increase in grid current.

Exercise 37

Fig. 49.



(a) From the graph, potential at ionization = 18.5 V

(b) First ionization energy $= 18.5\ V \times 96.3\ kJ\ mol^{-1}\ V^{-1}$

$= \boxed{1780\ kJ\ mol^{-1}}$

(strictly 1.78×10^{3} kJ mol^{-1}

(c) The first ionization energy of krypton is calculated by multiplying the ionization potential by the energy acquired by one mole of electrons moving through a potential difference of one volt.

$\therefore$ 1st I.E.(Kr) $= 14.0\ V \times 96.5\ kJ\ mol^{-1}\ V^{-1} = \boxed{1.35 \times 10^{3}\ kJ\ mol^{-1}}$

Note that this value would commonly be quoted as 1350 kJ mol^{-1} even though this implies greater precision than is justified.

Exercise 38

(a) $Al(g) \rightarrow Al^{+}(g) + e^{-}$

$Al^{+}(g) \rightarrow Al^{2+}(g) + e^{-}$

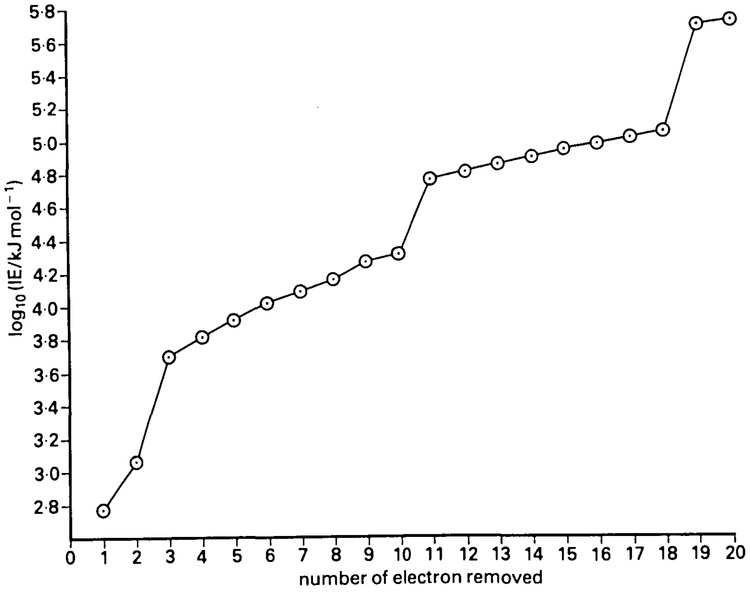
$Al^{2+}(g) \rightarrow Al^{3+}(g) + e^{-}$

(b) The values of the ionization energies increase in the order 1st < 2nd < 3rd

(c) Extra energy is needed to overcome the attractive forces between the leaving electrons and ions of increasing positive charge.

Exercise 39

(a) Fig. 50.



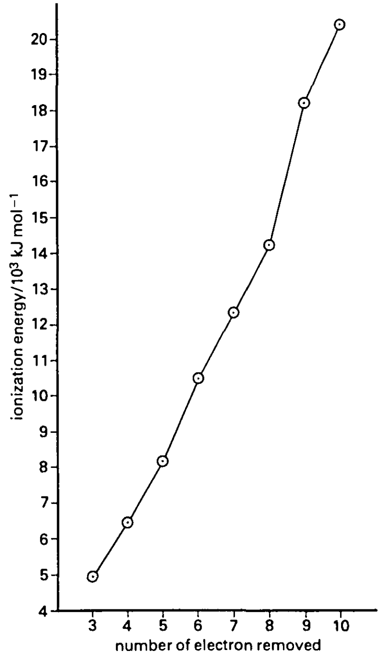
(b) The discontinuities in the graph indicate that there are two electrons in the outermost shell (with highest energy), eight electrons in each of the middle two shells and two electrons in the shell closest to the nucleus (with lowest energy).

(c) It would have been impossible to fit the non-logarithmic values all on a convenient scale. The first few values would be almost indistinguishable.

(d) The second electron is harder to remove than the first one as the attraction between the mono-positively charged ion and the outermost electrons has to be overcome. Successive electrons need increasing amounts of energy to remove them as the ion becomes increasingly positively charged.

Exercise 40

(a) Fig. 51



(b) The small jump between the eighth and ninth electrons indicate that the second electron shell is divided into two sub-shells, with two electrons at a lower energy level than the other six.

You may also see a slight discontinuity between the fifth and sixth electrons on your graph. The sixth electron is slightly more difficult to remove than extrapolation of the line suggests. We shall return to this idea later in the Unit.

(c) In the second shell, the electrons are arranged in two sub-shells. Two electrons, of lower energy, nearer the nucleus and six electrons, of higher energy, further from it.

Exercise 41

The orbital model is based on the probability of finding an electron in a given volume of space. It is not possible to state precisely where an electron will be at a given moment, only to define a region of space where there is a high probability that it will be located. Such a region of space is called an orbital.

Exercise 42

The second shell contains eight electrons.

The number of orbitals is n^2 and $n = 2$ for the second shell

$\therefore$ there are four orbitals

$\therefore$ number of electrons per orbital $= \frac{8}{4} = \boxed{2}$

Exercise 43

The subscripts x, y and z stand for the x, y and z axes and indicate the position the orbitals occupy in space relative to each other.

Exercise 44

(a) (i) 2 electrons.

(ii) 6 electrons.

(b) (i) Spherical.

(ii) Dumb-bell shaped.

Exercise 45

Table 7

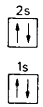
Shell	Number and type of orbitals	Maximum number of electrons in each set of orbitals	Maximum number of electrons in the shell
First shell	one *s*	2	2
Second shell	one *s* three *p*	2 6	8
Third shell	one *s* three *p* five *d*	2 6 10	18
Fourth shell	one *s* three *p* five *d* seven *f*	2 6 10 14	32

Exercise 46

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d

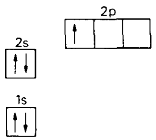
Exercise 47

$_4$Be

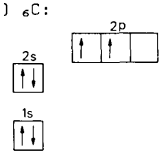


Exercise 48

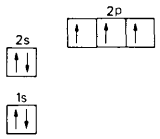
(a) $_5$B:



(b) $_6$C:

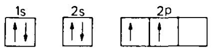


(c) $_7$N:

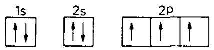


Exercise 49

(a) $_6$C:



(b) $_7$N:



Exercise 50

(a) (Ne)

(b) (Ne)

Exercise 51

(a) (Ne)$3s^2 3p^4$

(b) (Ne)$3s^2 3p^5$

(c) (Ne)$3s^2 3p^6$

Exercise 52

(a) (i) (He)$2s^2 2p^6$

(ii) (He)$2s^2 2p^6$

(b) Neon

Exercise 53

(a) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ or $(Ar)4s^1$

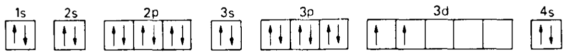
(b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ or $(Ar)4s^2$

Exercise 54

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$ or $(Ar)3d^1 4s^2$

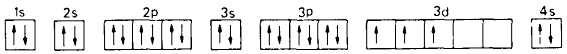
Exercise 55

(a) $_{22}Ti$ (i)



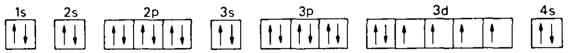
(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ or $(Ar)3d^2 4s^2$

(b) $_{23}V$ (i)



(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$ or $(Ar)3d^3 4s^2$

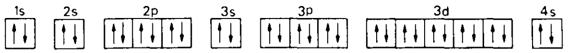
(c) $_{26}Fe$ (i)



(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ or $(Ar)3d^6 4s^2$

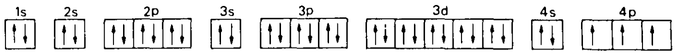
Exercise 56

(a) $_{31}Ga^+$ (i)



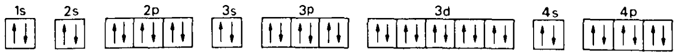
(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ or $(Ar)3d^{10} 4s^2$

(b) $_{33}As$ (i)



(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$ or $(Ar)3d^{10} 4s^2 4p^3$

(c) $_{35}Br^-$ (i)



(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ or (Kr)

Exercise 57

6s 4f 5d 6p

Exercise 58

(a) The *s*-, *p*-, *d*- and *f*- blocks are named after the last sub-shells to be filled in the build-up (aufbau) of these elements.

(b) No. The number of a period is the number of the quantum shell which starts to fill. However, the quantum shell is not completely filled by the end of Periods 4, 5 and 6: for example, the third shell is not completed till the end of Period 4. Summarising:

Period 4. 3*d* orbitals being filled in *d*-block elements

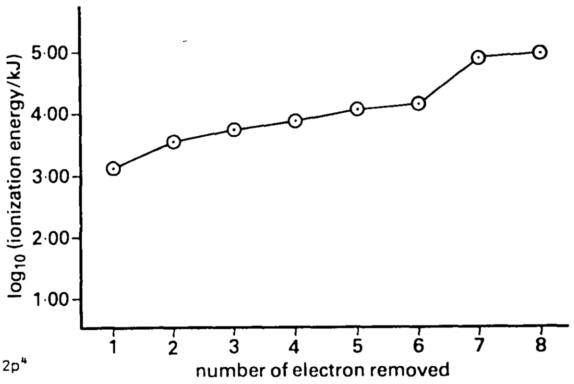
Period 5. 4*d* orbitals being filled in *d*-block elements

Period 6. 5*d* orbitals being filled in *d*-block elements

4*f* orbitals being filled in *f*-block elements

Exercise 59

(a) Fig. 52.



(b) $1s^2 2s^2 2p^4$

(c) Group VI

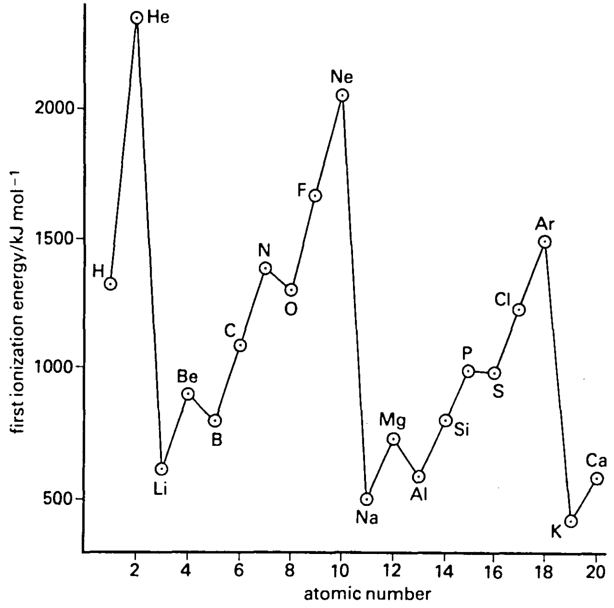
(d) X^{2-}

Exercise 60

(a) X (b) Y (c) Z

Exercise 61

Fig. 53



Experiment 2 - Question

A continuous spectrum shows a continuous range of wavelengths. In the visible range, this appears as broad bands of colour merging into one another with no sharp boundaries.

An emission spectrum shows a limited number of wavelengths, which appears as distinct lines. In the visible range, the lines appear in different colours.

Exercise 62

(a) Helium has one more proton in the nucleus than hydrogen. This increases the force of attraction on the electrons, which are both in the same shell, and makes it more difficult to remove one.

(b) The outer electron in the lithium atom is in a shell (*2s*) which is unoccupied in a helium atom. Despite the increased nuclear charge, the outer electron is relatively easy to remove for two reasons.

  (i) The inner electrons (*1s*) are interposed between the nucleus and the outer electrons, reducing the attractive force. This effect is known as 'shielding' or 'screening'.

  (ii) The outer electron is further from the nucleus in lithium than in helium. This also contributes to reducing the attractive force, but the reason given in (i) is more important.

(c) As in (b), there are two reasons:

  (i) The outer *2p* electron in boron is more effectively shielded from the nucleus by inner electrons than are the *2s* electrons in beryllium, despite the increased nuclear charge.

  (ii) The *2p* electron in boron is at a higher energy level than the *2s* electrons in beryllium and is therefore, on average, further from the nucleus.

(d) The three *2p* electrons in a nitrogen atom are unpaired, i.e. each *2p* orbital is singly occupied, and the mutual repulsion of these electrons is not great. However, in an oxygen atom, there is a pair of *2p* electrons, and since these two electrons experience mutual repulsion, it is easier to remove one of them than an unpaired electron.

(e) Each noble gas has the highest first ionization energy in its period. Moving from one noble gas to the next, the ionization energy decreases. In each case, the outer shell of electrons is further away from the nucleus and more effectively screened from it by the shells of lower energy. This decreases the effective nuclear charge and lowers the energy needed to remove an electron.

(f) The alkali metals have the lowest ionization energy in their respective periods. The explanation of the decrease in ionization energy in going from one alkali metal to the next is similar to that for the noble gases. In each case, the electron being removed is one shell further from the nucleus so that the effective nuclear charge is decreased and less energy is needed to remove the electron.

Exercise 63

(a) Wavelength is inversely proportional to frequency.

(b) $\lambda \propto 1/\nu$

Exercise 64

The energy of a quantum of radiation is proportional to its frequency. Ultraviolet rays have higher frequency and, therefore, more energy than infra-red rays. Ultraviolet rays have sufficient energy to damage body cells whereas infra-red rays do not.

Exercise 65

First, the frequency is calculated from the wavelength by substituting into the equation:

$$\lambda = \frac{c}{\nu} \text{ in the form } \nu = \frac{c}{\lambda}$$

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m s}^{-1}}{656.3 \times 10^{-9}\ \text{m}} = 4.57 \times 10^{14}\ \text{s}^{-1}$$

The energy is given by substituting into Planck's equation:

$$E = h\nu$$

$$\therefore E = 6.63 \times 10^{-34}\ \text{J s} \times 4.57 \times 10^{14}\ \text{s}^{-1} = \boxed{3.03 \times 10^{-19}\ \text{J}}$$

Alternatively, combining $\lambda = \frac{c}{\nu}$ with $E = h\nu$ and substituting,

$$E = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34}\ \text{J s} \times 3.00 \times 10^{8}\ \text{m s}^{-1}}{656.3 \times 10^{-9}\ \text{m}} = \boxed{3.03 \times 10^{-19}\ \text{J}}$$

Exercise 66

(a) The point where the spectral lines merge corresponds to electron transitions between $n = 2$ and $n = \infty$.

(b) If $n = \infty$, the electron has effectively left the atom.

(c) No. The energy value at this point is the energy required to remove an electron from the $n = 2$ level. Ionization energy is the energy required to remove an electron from its ground state, in this case the $n = 1$ level.

Exercise 67

(a) The lines in each series get closer together at higher frequencies.

(b) In each series, the high frequency lines are caused by electron transitions from the highest energy levels.

At high energies, the difference between energy levels gets smaller and smaller until they become indistinguishable.

Exercise 68

The Lyman series would be suitable for determining the ionization energy of hydrogen as it includes radiation emitted from electron transitions from the highest energy levels to the ground state.

Exercise 69

(a) The convergence limit represents the point at which an electron has gained enough energy to leave the atom completely. At this point, ionization has taken place. If the frequency of radiation corresponding to this point on the spectrum is known, the energy can be calculated using Planck's relationship, $E = h\nu$. This is the ionization energy of the atom.

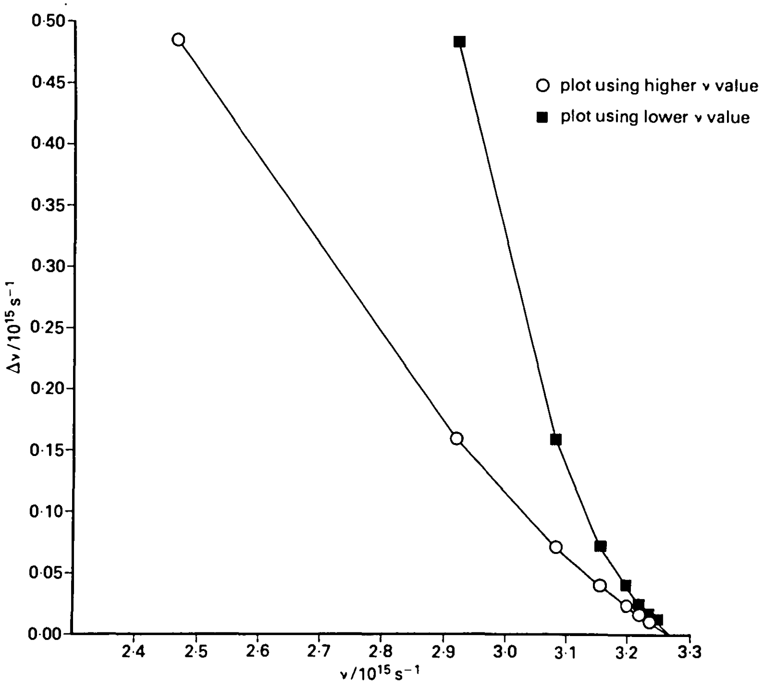
(b) The Balmer series is produced by electron transitions between higher energy levels and the $n = 2$ level; the Brackett series by transitions between higher levels and the $n = 4$ level. Neither series includes energy emitted during a transition from the highest level to the ground state. Unless appropriate adjustments are made, ionization energies calculated using the convergence limits of these series would be too low.

Exercise 70

Table 10

Energy level, n, of excited electron	Frequency, ν /10^{15} s^{-1}	$\Delta\nu$ /10^{15} s^{-1}	$\frac{1}{n^2}$
2	2.466	0.457	0.2500
3	2.923	0.160	0.1111
4	3.083	0.074	0.0625
5	3.157	0.040	0.0400
6	3.197	0.024	0.0278
7	3.221	0.016	0.0204
8	3.237	0.011	0.0156
9	3.248		0.0123

Fig. 54.



Exercise 70 (cont.)

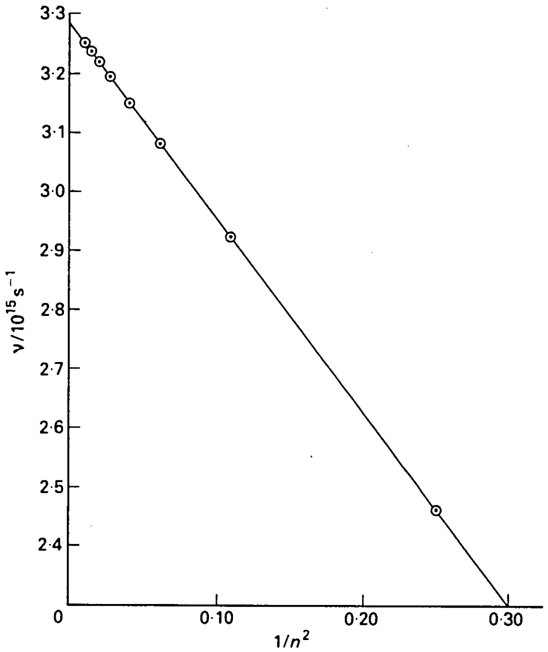


Fig. 55.

(a) (i) when $\Delta\nu = 0$, $\nu = 3.265 \times 10^{15}\ s^{-1}$

(ii) when $\Delta\nu = 0$, $\nu = 3.283 \times 10^{15}\ s^{-1}$

(b) Graph (i)

Substituting in the expression:

$$E = h\nu$$

gives $E = 6.63 \times 10^{-34}\ J\ s \times 3.265 \times 10^{15}\ s^{-1} = 2.165 \times 10^{-18}\ J$

For one mole, $E = 2.165 \times 10^{-18}\ J \times 6.02 \times 10^{23}\ mol^{-1} = 1.30 \times 10^{6}\ J\ mol^{-1}$

$\therefore$ ionisation energy $= \boxed{1.30 \times 10^{3}\ kJ\ mol^{-1}\ (1300\ kJ\ mol^{-1})}$

Graph (ii)

$E = 6.63 \times 10^{-34}\ J\ s \times 3.283 \times 10^{15}\ s^{-1} \times 6.02 \times 10^{23}\ mol^{-1}$

$= 1.31 \times 10^{6}\ J\ mol^{-1}$

$\therefore$ ionization energy $= \boxed{1.31 \times 10^{3}\ kJ\ mol^{-1}\ (1310\ kJ\ mol^{-1})}$

(c) Both graphs give values of ionization energy very close to the accepted value of 1310 kJ mol⁻¹. Method (ii) is somewhat more accurate because it is easier to extrapolate a straight line than a curve. However, even method (i) is considerably more accurate than the electron impact method.

(d) The Rydberg equation is

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

or $$\frac{\nu}{c} = R_H \left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

In the Lyman series, $n_2 = 1$ and we have put $n_1 = n$

Then $\frac{\nu}{c} = R_H \left(1 - \frac{1}{n^2}\right)$

or $\nu = -cR_H \left(\frac{1}{n^2}\right) + cR_H \qquad (y = mx + c)$

$\therefore$ slope of line $= -cR_H$ and intercept $= cR_H$

$$\text{Slope} = -\frac{(3.283 - 2.300) \times 10^{15}\ s^{-1}}{0.300} = -3.27 \times 10^{15}\ s^{-1}$$

$$\therefore R_H = -\frac{\text{slope}}{c} = \frac{3.27 \times 10^{15}\ s^{-1}}{3.00 \times 10^{8}\ m\ s^{-1}} = \boxed{1.09 \times 10^{7}\ m^{-1}}$$

Intercept $= 3.283 \times 10^{15}\ s^{-1}$

$$\therefore R_H = \frac{\text{intercept}}{c} = \frac{3.283 \times 10^{15}\ s^{-1}}{3.00 \times 10^{8}\ m\ s^{-1}} = \boxed{1.09 \times 10^{7}\ m^{-1}}$$

Exercise 71

$$\text{R.A.M.} = \frac{(34.97 \times 75.77) + (36.96 \times 24.23)}{100} = \boxed{35.45}$$

Exercise 72

$$\text{R.A.M.} = \frac{(7.4 \times 6.02) + (92.6 \times 7.02)}{100} = \boxed{6.95}$$

Exercise 73

$$\text{R.A.M.} = \frac{(62.9 \times 65) + (64.9 \times 35)}{100} = \boxed{63.6}$$

Exercise 74

$$\text{R.A.M.} = \frac{(60.4 \times 68.93) + (39.6 \times 70.92)}{100} = \boxed{69.7}$$

CONTRIBUTORS

Project Director

Colin Robertson, Inspector for Science, ILEA

Writing team

The materials were written and revised by practising teachers seconded to the Project for limited periods:

Lambros Atteshlis
Lesley Bulman
Mike Foley
Ann Friend
Lawrence Halstead
Terence Kelly
Frank McManus
Leonard Roselaar
Fran Rowe
Alec Thompson
Steve Waxman

Production Team

Tony Langham : i/c production and cover design
Vanda Chan : Graphics
John Sangwin : AVA Technician
Peter Faldon : AVA Technician
Dawn Devereux : Office and typing
Constance Godfrey: Typing
Stella Jefferies : Typing and layout

Videotapes

Brian Babb, Producer, Educational Television Centre, ILEA

Reader

John Stephens, Department of Natural Sciences, South London College

Evaluator

John Gilbert, Institute for Educational Technology, University of Surrey

ILPAC trial schools

The following schools and colleges took part in the trials of the Independent Learning Project for Advanced Chemistry. The Inner London Education Authority wishes to thank the teachers in these schools and their students for their help.

Abbey Wood School
Acland Burghley School
Bacon's C.E. School
Brooke House School
Dunraven School
Elliott School
Eltham Hill School
Ensham School
Forest Hill School
Highbury Grove School
Hull College of Further Education
Hydeburn School.
John Roan School
Ladbroke School
London Nautical School
Morpeth School
North Westminster Community School
Quintin Kynaston School
St. Mark's C.E. School
Sydenham School
Thomas Calton School
Walsingham School
Woodberry Down School
Woolverstone Hall

ILPAC

The *Independent Learning Project* for *Advanced Chemistry* is a comprehensive and detailed, yet flexible course of study designed to meet the requirements of *all* current Advanced Level GCE Chemistry syllabuses. It is also admirably suited for use with TEC and similar Further Education programmes in chemistry.

Extensive trials have proved ILPAC's efficiency as a route to examination success. But even more significant is the way in which ILPAC develops/ implants habits of independent study which are indispensable for post-A level work.

S2 Atomic Structure

This fundamentally important theme is dealt with at two Levels:
Level One concentrates on the atomic nucleus.
Level Two deals with the arrangement of extranuclear electrons. Atomic orbitals are approached through both electron bombardment and spectra, each illustrated by experiments. Treatment is straightforward and non-mathematical with emphasis on the importance of theoretical models in chemistry.

ILPAC UNITS

Starter Block

S1 The Mole
S2 Atomic Structure
S3 Chemical Energetics
S4 Bonding and Structure

Physical Chemistry

P1 The Gaseous State
P2 Equilibrium I: Principles
P3 Equilibrium II: Acids and Bases
P4 Intermolecular Forces and Solvation
P5 Chemical Kinetics
P6 Equilibrium III: Redox Reactions

Organic Chemistry

O1 Hydrocarbons
O2 Some Functional Groups
O3 More Functional Groups
O4 Big Molecules

Inorganic Chemistry

I1 s-Block Elements
I2 The Halogens
I3 The Periodic Table
I4 Group IV Elements
I5 Transition Elements
I6 Selected p-Block Elements

ISBN 0 7195 4036 4

John Murray