现代生物学精要速览 生物学中的化学 （影印版）

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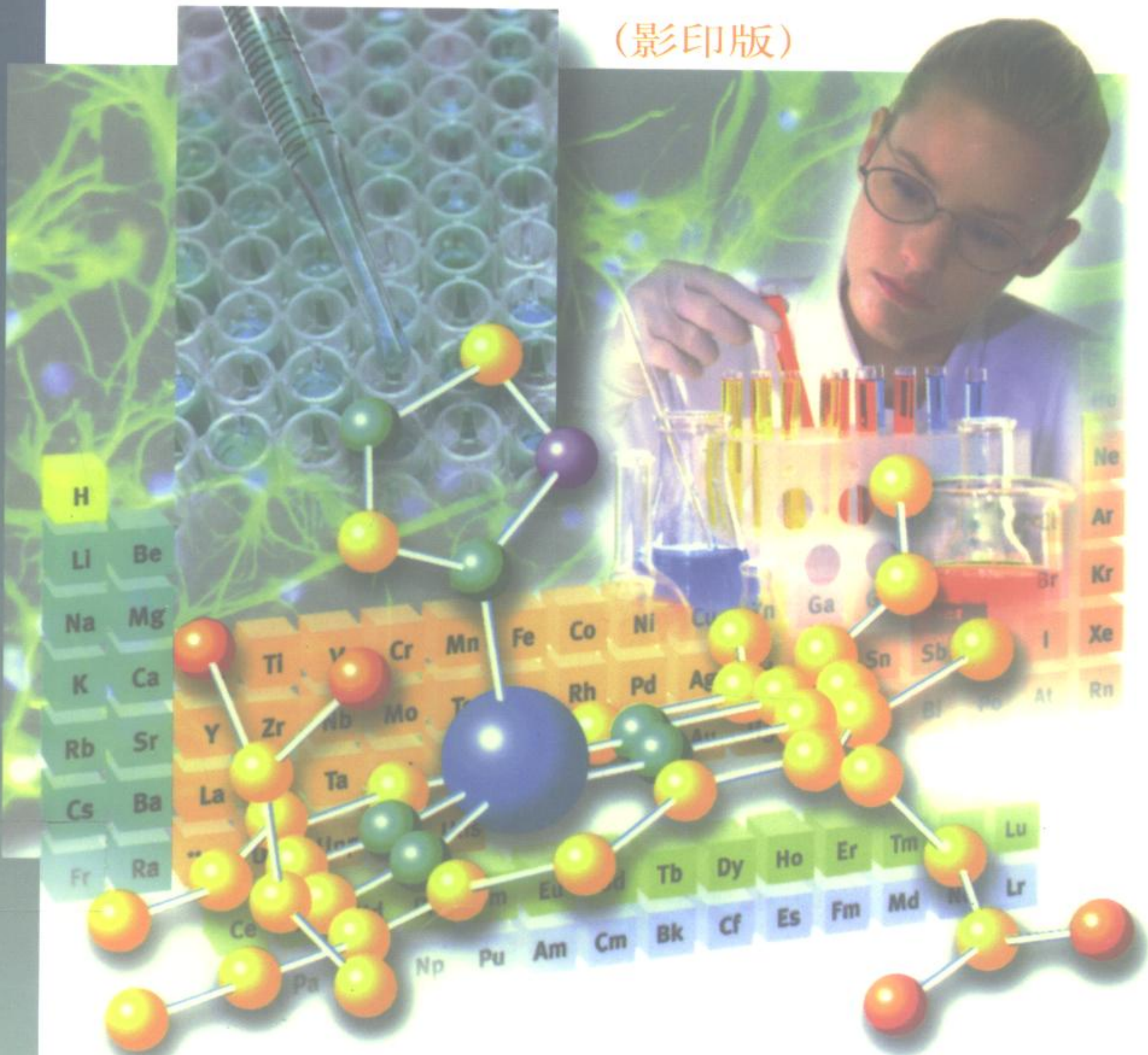
Instant Notes in

CHEMISTRY FOR BIOLOGISTS

生物学中的化学

(影印版)



J.Fisher & J.R.P. Arnold

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J.Fisher & J.R.P. Arnold

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University of Leeds, Leeds, UK

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内容简介

本套丛书是国外优秀教材畅销榜的上榜教材，面向大学本科生，由英国著名大学具有丰富教学经验的一流教授编写。它以一种风格独特的方式，全面、系统地概括了学科的核心内容和前沿动态，并以一种便于学习、利于复习的形式，使学生能快速、准确地掌握知识，很好地指导学习和考试。书中英文使用最为自然、易懂的语句，是提高专业外语的最佳套书。本书是该系列中的“生物学中的化学”分册，给生物系学生提供了应具备的化学知识的基本概念和大量的有用实例。

J. Fisher & J. R. P. Arnold
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ABBREVIATIONS

ADP	adenosine diphosphate
ATP	adenosine triphosphate
Bq	Becquerel
CI	chemical ionization
Ci	Curie
d	dextrorotatory (clockwise)
DCCI/DCCD	dicyclohexylcarbodiimide
DMT	dimethoxytrityl
E	entgegen (opposite)
E1	unimolecular elimination
E2	bimolecular elimination
Ea	activation energy
EI	electron impact
EM	electromagnetic
ESI	electrospray ionization
FAB	fast atom bombardment
FAD	flavin adenine dinucleotide
fid	free induction decay
FT	Fourier transform
G	Gibbs free energy
Gy	Gray
HOMO	highest occupied molecular orbital
IR	infrared
IUPAC	International Union of Pure and Applied Chemistry
l	levorotatory (anticlockwise)
LCAO	linear combination of atomic orbitals
LUMO	lowest unoccupied molecular orbital
MO	molecular orbital
MS	mass spectrometry
NAD^+	nicotinamide adenine dinucleotide (oxidized form)
NADH	nicotinamide adenine dinucleotide (reduced form)
NMR	nuclear magnetic resonance
nOe	nuclear Overhauser effect
[O]	oxidizing agents
OH	hydroxyl group
R	rectus (clockwise, chiral center)
S	sinister (anticlockwise, chiral center)
SN1	unimolecular nucleophilic substitution
SN2	bimolecular nucleophilic substitution
TBDMS	tertiary butyl dimethylsilyl
u	atomic mass unit
UV	ultraviolet
Z	zussamen (together)

PREFACE

Students of the biological sciences require a good grounding in chemistry if they are to fully understand key aspects of their courses. Many, but not all, students choosing to study biology, biochemistry and the like, have studied chemistry to 'advanced' level or equivalent. However, the knowledge gained at this stage is generally quickly forgotten, does not usually go far enough or it does not make relevant connections to biological systems. There are of course numerous excellent texts available which cover in great detail many of the topics which impinge on the biological sciences. Some of these attempt to set the material in a biological context. For the most part students studying chemistry as a subsidiary subject often find such texts overwhelming. A number of books have been written on chemistry aimed specifically at biological or life sciences students, and these are a useful source of reference. However, in general we have found that these do not cover the material that we require our biological sciences students to learn. As the number of such students at Leeds is currently over 400 each year we felt it worthwhile writing this book.

Instant Notes in Chemistry for Biologists aims to cover all aspects of chemistry relevant to the biological sciences and is based largely on the contents of the lecture course given by both chemistry and biochemistry departments at the University of Leeds. The book is divided into 15 sections containing 52 topics. Each topic consists of a Key Notes panel with concise statements of the key points covered. These are expanded on in the main part of the topic which includes simple and clear black and white figures which may readily be reproduced for essays or examinations for example. The key notes are essentially a revision aid hence the main body of the text is best read first. The ordering of the topics reflects the fact that some fundamental principles need to be learnt at the outset. Once the early sections have been digested the later topics may be dipped into subsequently. The topics are extensively cross-referenced to assist learning and understanding.

The contents of the book includes aspects of organic, inorganic and physical chemistry. In some instances the division between these branches of chemistry is obvious, in others less so. We have endeavored to cover material in a manner appropriate to the biological sciences and in doing so break down unnecessary divides. Section A provides an introduction to key features of the elements, from atomic structure, to the periodic table, through to isotopes: including natural and synthetic radioisotopes. This leads to Section B and the description of bonding and molecular shape and how these may be represented on paper. In Section C the properties of water and phosphoric acid are discussed in terms of chemistry but as examples of extremely biologically important small molecules. The vast majority of all other biological molecules are carbon based and consequently Section D is aimed at explaining why life should have evolved based on this element.

Section E introduces the concept of isomerism, paying particular attention to stereoisomerism and the labeling of absolute 3-dimensional structures of stereoisomers.

In Section F the emphasis shifts from molecules of importance to the elements, particularly metals of importance in biology.

A key feature of many biochemical polymers is the network of weak interactions which hold large structures together, such as hydrogen bonds and hydrophobic interactions. These are discussed in Section G.

In Section H definitions are provided for the various reactive species in chemical reactions. Mechanisms and factors influencing these are included. This leads naturally to Section I in which the key properties of functional groups which frequently occur in biochemistry are discussed. In Section J a similar approach is adopted in considering a special functional group, the aromatic ring. This then leads to section K in which the chemical synthesis of biochemical polymers is described.

Section L covers acid-base properties of aqueous solutions, with a description of buffer solutions and the concept of solubility.

In Section M the fundamentals of thermodynamics are set out. This is a necessary prelude to Section N in which rates of reaction, enzyme kinetics and catalysis in general are discussed.

Finally in Section O the principle of quantitization of energy is introduced together with a description of the electromagnetic spectrum. The information available from the application of various components of this spectrum; ultraviolet, infrared and radiowaves is also covered.

This book is not intended to provide an in depth coverage of chemical concepts, such as books included in the Further Reading list, but rather an overview of key biochemically relevant material. It will work well with other books in this series, in particular *Instant Notes in Biochemistry.*

Julie Fisher, John Arnold

To Elizabeth and Abigail

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A1 THE PERIODIC TABLE

Key Notes

Atomic structure	The atom consists of a nucleus containing protons and neutrons and is surrounded by electrons. Electrons are located in specific energy shells and discrete packets, or quanta, of energy are required for electrons to move from one shell to another. The number of protons found at the nucleus is defined as the atomic number.
Atomic orbitals	The electrons which surround the nucleus of an atom occupy regions of space referred to as orbitals, or subshells. The size of the nucleus and the number of electrons determines the shape and overall energy of a particular orbital. These orbitals are labeled 1s, 2s, 2p, 3p, 4d, 5f, etc. The letter refers to the shape of the orbital, the number to the shell location.
Periodicity	Properties such as valency (number of electrons in the outer shell), and electronegativity (electron-withdrawing or attracting power) of the elements vary in a regular manner according to atomic number. The periodicity of these properties is reflected in the arrangement of rows and columns in the periodic table.

Related topics

Electron configuration (A2)
Isotopes (A3)
Molecular orbitals (B1)
The early transition metals (F1)

Atomic structure

At the turn of the 18th century, the generally held view of the atom was that put forward by John Dalton. His atomic theory had as its basis that atoms were indestructible. It was not until around the turn of the 19th century that this was shown to be incorrect. Atoms are actually comprised of **subatomic particles** known as **neutrons, protons,** and **electrons.** The bulk of the mass of the atom is made up of the mass of the neutrons and protons, each given an atomic mass of 1,the mass of the electron being negligible. The neutron has no charge whereas the proton has a single positive charge and the electron a single negative charge:

Hence, the (neutral) atom has the same number of electrons as protons. As the number of protons does not vary for a particular element (see Topic A3) the **number of protons** is the **atomic number** . It was not until the end of the 19th century that the organization of these particles with respect to each other was determined. Experiments involving bombarding metal films with the subatomic particles emitted by various **radioisotopes** (see Topic A3) revealed that the atom had a core or **nucleus** where the bulk of its mass was housed; the neutrons, protons and electrons must therefore occupy space surrounding the nucleus.

In 1913 the Danish physicist Niels Bohr postulated that electrons were not simply free to circulate around the nucleus but instead that they must occupy specific allowed energy states; referred to as **energy levels or shells.** Discrete packets of energy, or **quanta** (see Topic O1), are expelled or absorbed to move an electron

Table 1. *Electron occupancy of principal shells*

	Low energy ———►				High energy
Energy shell	1	2	3	4	5
Electron capacity	2	8	18	32	32
Number orbitals	s	s, p(x3)	s, p(x3), d(x5)		

from one principal shell to another. There is a maximum number of electrons that can occupy each shell (see *Table 1*)

Atomic orbitals

Within each electron shell there are **subshells**. These subshells have a degree of 'fine structure', in that there are specific locations within the subshell where there is a higher probability of finding an electron than in other regions. These regions are referred to as **atomic orbitals**. These orbitals have unique shapes and can hold two electrons provided these electrons are spinning in opposite directions (see Topic A2). The shapes of the orbitals are specified by the letters 's', 'p', 'd', and 'f' etc., and are shown in *Fig. 1*.

Different energy levels have different numbers of these orbitals as shown in *Table 1*.

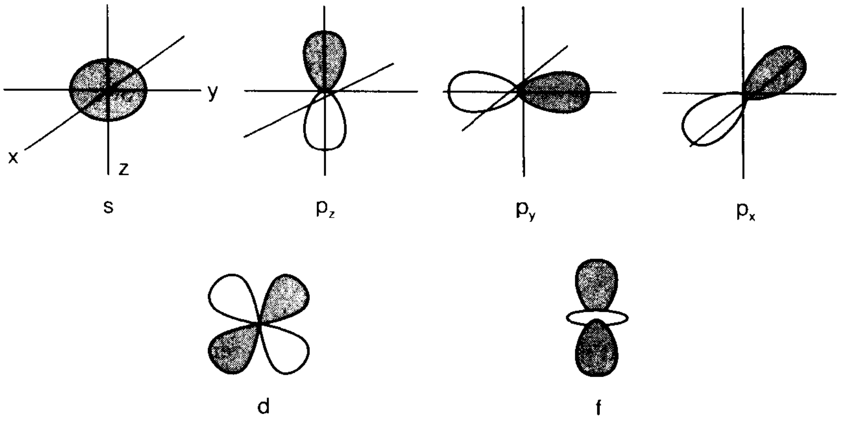

Fig. 1. *Shapes of some of the atomic orbitals. There are three 'p' orbitals in the x,y,z directions and five 'd' orbitals in each shell where these appear.*

Periodicity

Mendeleev in the mid-1800s noted that various properties of the elements seem to go through cycles as atomic number is increased. The boiling points, for example, do not increase with atomic number but go through peaks and troughs (see *Fig. 2*).

The energy required to remove an electron (the ionization energy) followed a similar trend (see *Fig. 3*)

Also it was noted that the number of bonds that an element could form with another element varied with atomic number (see Topic B2 and *Table 2*).

An atom of an element with atomic number 3, 11 or 19, is able to combine with one atom of some other element, and is thus referred to as **monovalent**. Those with atomic numbers 5 and 13 are able to form three bonds and are referred to as being **trivalent** elements, and so on. It should be noted that elements with atomic

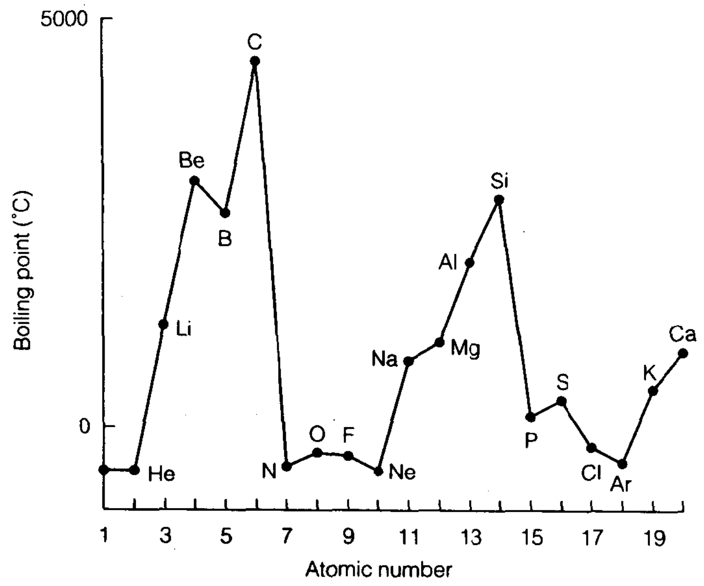

Fig. 2. Variation of boiling point with atomic number.

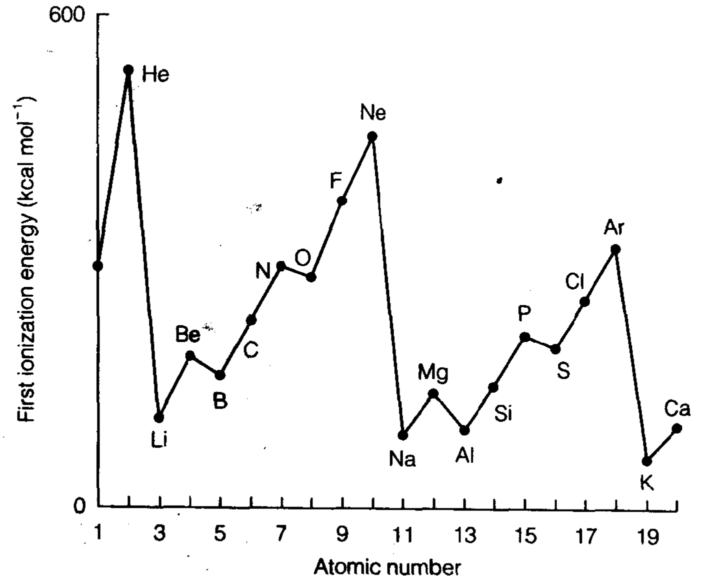

Fig. 3. Variation of first ionization energy with atomic number.

numbers 2, 10 and 18 etc. do not readily form bonds with other elements. This is due to the fact that these elements have a complete outer shell of electrons which makes them very stable. Indeed these elements are called the **inert** or **noble** gases.

These trends are of course all reflected in the modern organization of the periodic table (see *Fig. 4*).

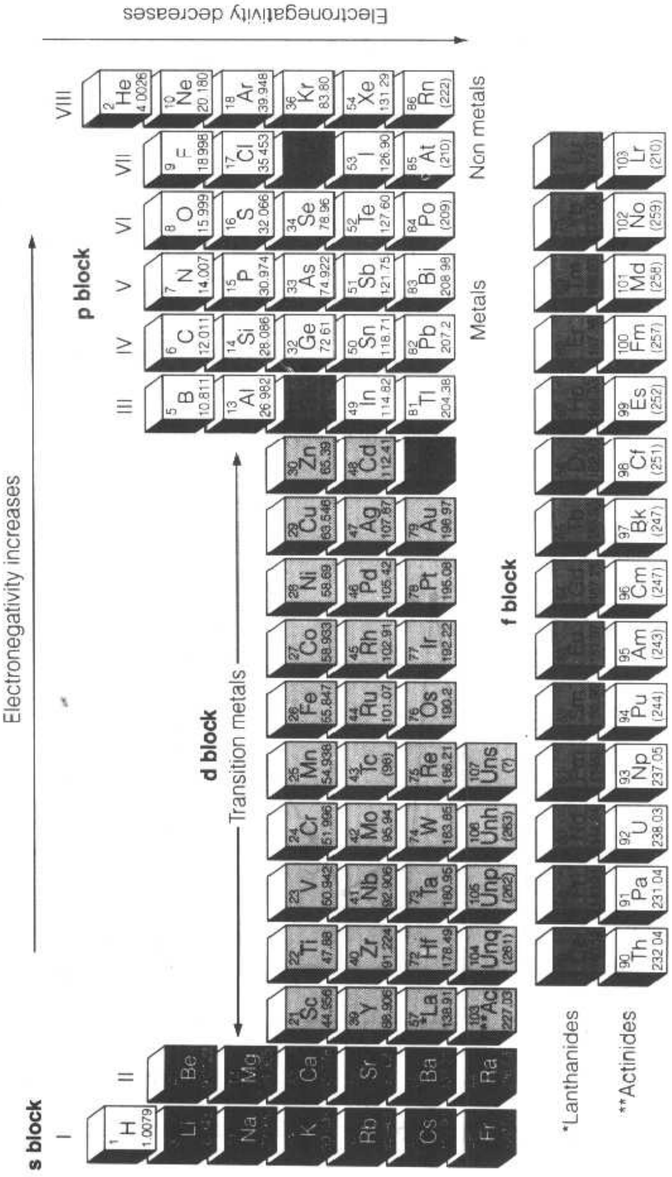

Fig. 4. *The periodic table of the elements.*

Table 2. Variation of bond capacity with atomic number

Atomic number		No. of bonds	Example	
(a)	(b)		(a)	(b)
3,	11	1	LiH	NaH
4,	12	2	BeH_2	MgH_2
5,	13	3	BH_3	AlH_3
6,	14	4	CH_4	SiH_4
7,	15	3	NH_3	PH_3
8,	16	2	OH_2	SH_2
9,	17	1	FH	ClH
10,	18	0	–	–

The periodic table is arranged in columns. In each column the elements have the same outer shell **electronic configuration** (see Topic A2) and therefore the **same valence**. As illustrated in *Fig. 3*, elements in Group I require the input of a relatively small amount of energy to lose an electron, i.e. to ionize. This readiness to lose an electron has led to these and the Group II elements being termed **electropositive**.

In contrast, it is extremely difficult to remove an electron from the Group VII elements; these are close to the stable complete outer shell position and therefore have a stronger tendency to acquire electrons. Consequently these elements are referred to as being **electronegative**.

It is the ability of an element to lose or accept electrons that dictates its chemistry (see Topic B2).

A2 ELECTRON CONFIGURATION

Key Notes

Aufbau principle	The word 'aufbau' is German for 'building up'. The aufbau principle states that the lowest energy orbital will be the first filled with electrons.
Pauli exclusion principle	The Pauli exclusion principle states that only two electrons may be placed in each orbital and these electrons must have opposed spins.
Hund's rule	Hund's rule states that if two or more empty orbitals of equal energy are available, one electron must be placed in each orbital until they are all half-filled.
Abbreviated configuration	A shorthand method for describing the electronic configuration of an atom has been developed. For example, $1s^1$ and $1s^2$, signify that 1 and 2 electrons, respectively, are present in the 1s orbital.
Related topics	Molecular orbitals (B1) Nature of chemical bonding (B2)

Aufbau principle

The arrangement of electrons in atomic or molecular orbitals (see Topic B1) is known as the **electronic configuration**. In determining the electronic configuration a number of rules have to be considered. The first is that the **lowest energy orbital must be filled first**. Therefore, all atoms have electrons in the 1s level, and so on. This is the known as the **aufbau principle**.

Pauli exclusion principle

The Pauli exclusion principle states that each orbital has a maximum occupancy of two electrons. An electron has a property called a **spin**, and can be thought of as rotating about an axis. Of course it can rotate from west to east or east to west, therefore it has two possible orientations, or two spins. These are denoted as an up (↑) and down (↓) arrow. The Pauli exclusion principle states that two electrons in the same orbital must have opposite spins (see *Fig. 1*).

Hund's rule

Each electron shell is at a different energy level. Within each shell there are the **subshells** called **atomic orbitals** (see Topic A1). From shell 2 onwards, more than one orbital type is present. In level 2 there is one 's' and three 'p' orbitals. The 'p' orbitals are all at the same energy level, (the 's' orbital slightly lower) and are thus referred to as being **degenerate**. Hund's rule says that if there are two or more degenerate orbitals then these should be singly occupied until they are all half filled.

Using the aufbau, Pauli and Hund rules it is possible to write the electron configurations of the ground state, the lowest energy state, of all the elements (see *Fig. 2*).

	1s	2s	2p	2p	2p
H	↑				
He	↑↓				
Li	↑↓	↑			
Be	↑↓	↑↓			
B	↑↓	↑↓	↑		

Fig. 1. Organization of electrons in atomic orbitals according to the Pauli exclusion principle.

	1s	2s	2p	2p	2p
C	↑↓	↑↓	↑	↑	
N	↑↓	↑↓	↑	↑	↑
O	↑↓	↑↓	↑↓	↑	↑
F	↑↓	↑↓	↑↓	↑↓	↑
Ne	↑↓	↑↓	↑↓	↑↓	↑↓

Fig. 2. Organization of electrons in atomic orbitals following the Pauli exclusion principle and Hund's rule.

Abbreviated configuration

The format adopted in *Fig.* 2 for electronic configurations is somewhat cumbersome. It is more convenient to 'abbreviate' this picture as shown in *Fig.* 3. Clearly the configuration for boron ($1s^2\ 2s^2\ 2p^1$) signifies 2 electrons in the 1s orbital, 2 in the 2s and 1 in the p orbitals. A further abbreviation is possible by referring to the previous inert gas. Thus, the electronic configuration of lithium is, with reference to helium, (He) $2s^1$ (see *Fig.* 3).

H	$1s^1$		
He	$1s^2$		
Li	$1s^2$	$2s^1$	
Be	$1s^2$	$2s^2$	
B	$1s^2$	$2s^2$	$2p^1$
C	$1s^2$	$2s^2$	$2p^2$
Li	(He)	$2s^1$ (i.e. the configuration of helium plus a 2s electron)	
Na	(Ne)	$2s^1$ (i.e. the configuration of neon plus a 2s electron)	

Fig. 3. Some abbreviated electronic configurations.

A3 ISOTOPES

Key Notes

Definition	Atoms which have the same number of protons but differing numbers of neutrons are referred to as isotopes of each other.
The mole	One mole of any element or compound has the identical number of formula units as atoms that are present in 12.0000 g of carbon-12.
Stable isotopes	Stable isotopes are those which under normal conditions do not transform into other element types. They do not require special handling.
Radioisotopes	Radioisotopes are isotopes that decompose and in doing so emit harmful particles and/or radiation. There are naturally occurring radioisotopes (e.g. ^{238}Ur) and those that may be prepared synthetically (e.g. ^{3}H, ^{32}P).
α-emitters	Isotopes which emit a particle consisting of 2 protons and 2 neutrons (the nucleus of Helium) are referred to as α-emitters and the unit of mass number 4 is an α-particle.
β-emitters	Isotopes whose nuclei can lose an electron are referred to as β-emitters and the stream of electrons emitted from the nucleus are referred to as β-particles.
γ-emitters	Isotopes which emit a photon of energy in addition to losing particles of β- or α-radiation are referred to as γ-emitters. As the energy has no mass this is referred to as γ-radiation rather than γ-particles.
Half-life	The half-life is the time required for the activity of a radioisotope to have decayed to 50% of the original activity.
Units and measurement	The unit of activity of radiation is the Becquerel (Bq), and the unit of dose is the Gray (Gy). Film dosimeters, Geiger counters, and scintillation counters are all used to measure radiation.
Radiation damage and sickness	Alpha and β-particles, and X-rays and γ-rays cause the formation of unstable ions or free radicals when they pass through the body. These highly active species can modify the cells genetic material and lead to a range of symptoms; from nausea to cancers.
Use of radioisotopes	Radioisotopes are used in the food industry for prolonging product life. In biological sciences they are used as an analytical tool, and in medicine as a diagnostic tool.

Related topics The periodic table (A1) Electron configuration (A2)