

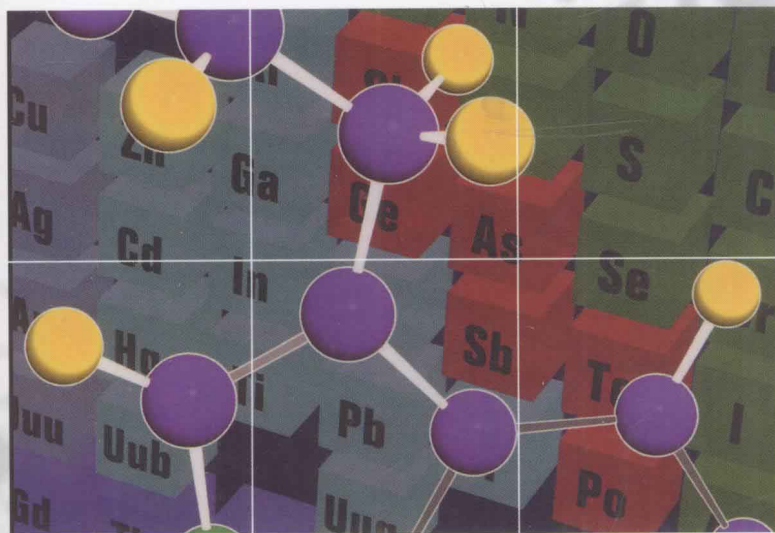
精要速览系列

Instant Notes

CHEMISTRY FOR BIOLOGISTS

(SECOND EDITION)

生物学中的化学 (第二版)



· 导读版 ·

J.Fisher & J.R.P.Arnold



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精要速览系列
Instant Notes in

Chemistry for Biologists

Second Edition

生物学中的化学

(第二版, 导读版)

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内 容 简 介

“精要速览系列(*Instant Notes Series*)”丛书是国外教材“Best Seller”榜的上榜教材。该系列结构新颖,视角独特,重点明确,脉络分明;图表简明清晰;英文自然易懂,被国内多所重点院校选用作为双语教材。

第二版在第一版基础上进行修订,涵盖化学学科主要概念,简析重要术语,通过生物学事例解释其化学原理。第二版新增加改动比较大的内容包括水,生物体系的溶剂;生物学中重要的小分子;重要的生物大分子;热力学;园二色等。

本书适合普通高等院校生命科学、医学、农学等相关专业使用,也可作为双语教学参考教材使用。

J. Fisher, J. R. P. Arnold

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第二版前言

本书第一版出版的这三年中,我们收到了大量关于本书内容及风格的反馈,令人高兴的是大部分反馈都是称赞本书!在我们读到的反馈中有一些是关于修改或增加内容的建议。我们在新版中采纳了这些建议,同时也增加了一些自认为有助于读者理解本书的内容。一些比较大的改进罗列如下:

作为生物学家及相关学者的用书,鉴于水是生物体系的溶剂,因此我们(在 C 部分)增加了更多的内容,用以描述水这种溶剂是如何奇特的,以及为什么会这么奇特。在这一版中还加入了生物学中重要的小分子部分(F 部分),在此部分中阐述了氮分子和氧分子,在上一版中这两个分子仅在金属部分(G 部分)一带而过,而没有专门论述。第一版中核酸和蛋白质只是在介绍它们的单体时顺便提及,在这一版中我们有机会增加蛋白质和核酸的内容,与此同时,还同时引入关于脂的内容(形成了 K 部分)。在重新审视热力学部分时,我们修改了关于吉布斯自由能和熵的统计学定义。最后,为了内容的完整,我们在谱学部分加入了圆二色的内容,因为 CD 是结构生物化学中非常有用的技术。本书作者及许多审稿人,都认为这个专题应该放在化学家们常用的谱学技术之外。

一如既往地献给伊丽莎白及阿尔盖尔!

PREFACE TO SECOND EDITION

In the 3 years that have passed since the publication of the first edition we have received significant feedback on the book's content and style. Happily the majority of this has been very favourable! Amongst the comments we have read have been a few suggestions for modifications or additions to the text. We have taken note of these in preparing this new edition, whilst also incorporating some changes we ourselves felt would improve the readers understanding. A number of the more significant changes are outlined below.

As the book is for biologists and the like, and as water is the biological solvent, we have provided (in Section C) more information about how and why this solvent is so unique. We now include a section on small inorganic molecules of biological interest (Section F) which permits us to cover molecular nitrogen and molecular oxygen, previously not considered except in passing in the section on metals (Section G). In the first edition nucleic acids and proteins were mentioned in terms of their building blocks. We have taken the opportunity with this new edition to include information regarding their respective roles. In doing this we thought it sensible to consider other biological macromolecules, hence we have included a topic covering the composition and function of lipids (Section K). We have looked again at the section on thermodynamics and have made some modifications to our discussion of Gibb's free energy and the statistical definition of entropy. Finally, for completeness we have included a description of circular dichroism in the section on spectroscopy (Section Q). CD is a very useful technique in structural biochemistry. We, in common with a number of reviewers, felt this topic should be presented alongside the spectroscopic techniques more commonly used by chemists.

For Elizabeth and Abigail, as always!

第一版前言

学习生物学的学生如果想对他们课程中的关键概念有全面的了解,就需要在化学方面打好基础。现在许多选择学习生物学、生物化学等专业的学生通常直接学习高等化学或类似的化学课程。然而,在这个层次上学习的知识很容易忘记,而且这些知识并不足以或不能与生命体系发生联系。当然还有许多涉及生命科学内容的课程,它们也都很出色,其中一些课程的内容成为生物学教程的材料。但是那些以化学为辅修学科的学生学习这些课程时感到很头痛。现在有许多专门为学习生物和生命科学的学生写的化学书,都是很有用的参考资料。然而,我们发现通常这些书并不包含我们希望学习生物的学生学习的所有知识。在利兹(Leeds)市,每年大约有 400 多名这样的学生,这使我们感到十分有必要写这样的一本书。

《生物学中的化学》包括了与生命科学有关的所有化学知识,主要来自利兹大学生物系和化学系提供的教案。全书共分 15 部分,52 个主题。每一个主题都有“要点”部分,它简要介绍了本节的主要内容。在每个主题的正文中,要点部分的内容被扩展。正文中有许多简明清晰的黑白插图,可以帮助说明所举的例子。要点部分概括性较强,所以阅读时应首先读正文。由章节的安排可以看出许多基本定律应该先学习。一旦前面的知识了解了,后面的内容就很容易理解。许多章节的内容被交叉引用,以便理解。

本书包括有机化学、无机化学和物理化学三个方面。有些章节中,这三个化学分支学科的界限很明显,而其他情况下则很模糊。我们努力将素材以接近生命科学的方式引入,尽量消除不必要的界限。A 部分从原子结构到元素周期表,对元素的主要方面进行系统的介绍。还介绍了同位素,包括天然同位素和人工合成的同位素。接着引出了 B 部分,主要介绍键和分子形状的描述及它们如何在纸面上表达。C 部分介绍了生命体系中重要的小分子——水和磷酸的性质。生物分子几乎都含有碳,接着 D 部分着重解释为什么生命以这种元素为基础。

E 部分主要介绍了异构现象,其中着重介绍了立体异构及立体异构体三维结构的抽象标记方法。

F 部分将焦点从分子移到元素,着重介绍了金属在生物学中的重要意义。

许多生化高分子化合物的主要性质是它们的庞大结构由弱相互作用力维持,如氢键、疏水相互作用等。这些将在 G 部分介绍。

H 部分主要介绍了化学反应中的各种活性物质,以及它们的机理和影响因素。接着 I 部分主要介绍了生物化学中常见的一些官能团的主要性质。J 部分着重介绍了一种特殊的官能团——芳香基。而后,K 部分介绍了生化高分子化合物的化学合成方法。

L 部分主要介绍水溶液中的酸碱性质,还介绍了缓冲剂和溶解度的概念。

M 部分主要介绍化学热力学的基本知识,这是 N 部分的前奏。N 部分主要介绍反应速率、一般的酶动力学和酶催化反应。

谨此献给伊丽莎白和阿尔盖尔

PREFACE TO FIRST EDITION

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 quantization of energy is introduced together with a description of the electromagnetic spectrum. The information available from the application of various components of this spectrum; ultra-violet, 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

缩略词

ADP	adenosine diphosphate	二磷酸腺苷
ATP	adenosine triphosphate	三磷酸腺苷
Bq	Becquerel	贝可
CD	circular dichroism	圆二色
CI	chemical ionization	化学电离
Ci	Curie	居里
<i>d</i>	dextrorotatory(clockwise)	<i>d</i> 构型(顺时针)
DCCI/DCCD	dicyclohexylcarbodiimide	二环己基碳二亚胺
DMT	dimethoxytrityl	二甲氧基三苯甲基
E	entgegen(opposite)	E 构型(异侧)
E1	unimolecular elimination	单分子消除反应
E2	bimolecular elimination	双分子消除反应
E _a	activation energy	活化能
EI	electron impact	电子轰击
EM	electromagnetic	电磁波
ESI	electrospray ionization	电喷雾
FAB	fast atom bombardment	快原子轰击
FAD	flavin adenine dinucleotide	黄素腺嘌呤二核苷酸
fid	free induction decay	自由感应衰减信号
FT	Fourier transform	傅里叶变换
G	Gibbs free energy	吉布斯自由能
Gy	Gray	戈瑞
HOMO	highest occupied molecular orbital	最高占据分子轨道
IR	infrared	红外
IUPAC	International Union of Pure and Applied Chemistry	国际纯粹与应用化学会
<i>l</i>	levorotatory(anticlockwise)	<i>l</i> 构型(逆时针)
LCAO	linear combination of atomic orbitals	原子轨道线性组合
LUMO	lowest unoccupied molecular orbital	最低未占有分子轨道
MO	molecular orbital	分子轨道
MS	mass spectrometry	质谱
NAD ⁺	nicotinamide adenine dinucleotide(oxidized form)	尼克酰胺腺嘌呤二核苷酸(氧化型)
NADH	nicotinamide adenine dinucleotide(reduced form)	尼克酰胺腺嘌呤二核苷酸(还原型)
NMR	nuclear magnetic resonance	核磁共振
nOe	nuclear Overhauser effect	核欧沃豪斯效应
[O]	oxidizing agents	氧化剂
OH	hydroxyl group	羟基

ORD	optical rotatory dispersion	旋光光谱
R	rectus(clockwise, chiral center)	R 构型(顺时针, 手性中心)
S	sinister(anticlockwise, chiral center)	S 构型(逆时针, 手性中心)
SN1	unimolecular nucleophilic substitution	单分子亲核取代反应
SN2	bimolecular nucleophilic substitution	双分子亲核取代反应
TBDMS	tertiary butyl dimethylsilyl	叔丁基二甲基硅烷基(羟基保护基)
u	atomic mass unit	原子质量单位
UV	ultraviolet	紫外线
Z	zusammen(together)	Z 构型(同侧)

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第一版前言

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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.

Quantum mechanics

The idea that electrons resided in specific allowed energy states proved very useful in explaining some physical observations. However, why electrons should be distributed in this way was not explained until the principle of wave-particle duality was developed. The wave-like behavior of electrons is termed quantum mechanics.

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 (G1)

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 Q1), are expelled or absorbed to move an electron from one principal shell to another. There is a maximum number of electrons that can occupy each shell (see Table 1)

Table 1. Electron occupancy of principal shells

	Low energy \longrightarrow 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)		

Quantum mechanics

Bohr's model of the atom was highly successful, especially in predicting the emission spectrum of the hydrogen atom. However, it provided no underlying reason as to just *why* electrons should be layered in shells within atoms. The answer came from **wave-particle duality**. During the early part of the 20th century, a number of experimental observations were made in which electrons behaved as if they were classical particles, whilst on other occasions they acted as if they were waves. The wave-like character of electrons was evident, for example, in the patterns formed by beams of electrons passing through crystals. This mixture of characteristics has caused philosophical problems ever since, as it became evident during the 1920s that sub-atomic matter had a strange, fuzzy existence; Einstein was not satisfied by this, but was unable to devise a more satisfactory description. In general, a particle can be described by a wave, the amplitude (or strictly, the amplitude²) of which is related to the probability of finding the particle at a given position. The wave-like behavior is termed **quantum mechanics**, or sometimes **wave mechanics**. The wave is a mathematical function, often called the wave function. This function strongly depends on the physical forces acting on the particle, usually these are electrostatic influences of nuclei and/or electrons. So, when a negatively charged electron is associated with a positively charged proton (as in the hydrogen atom), the electrostatic attraction between the two causes only certain electron wave functions to be allowable. These gave rise to atomic orbitals, which are grouped in shells, just as in the Bohr model.

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.

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,

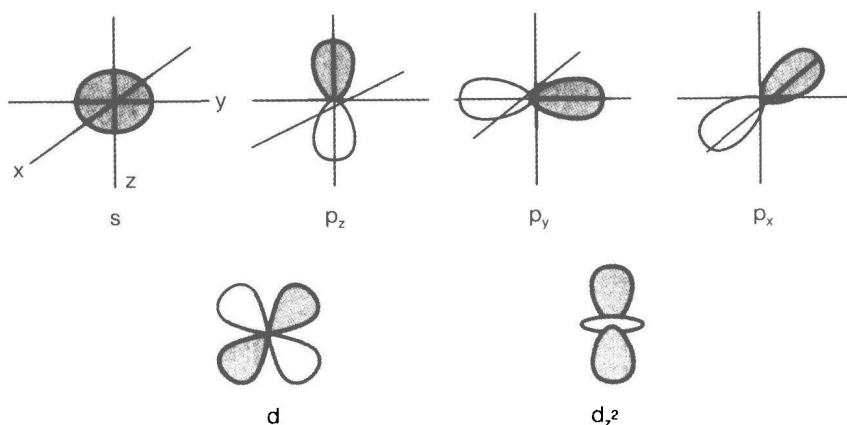


Fig. 1. Shapes of some of the atomic orbitals. There are three 'p' orbitals in the x,y,z directions and five 'd' orbitals in each shell where these appear. Orbitals show boundaries within which 95% probability of finding electron.

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

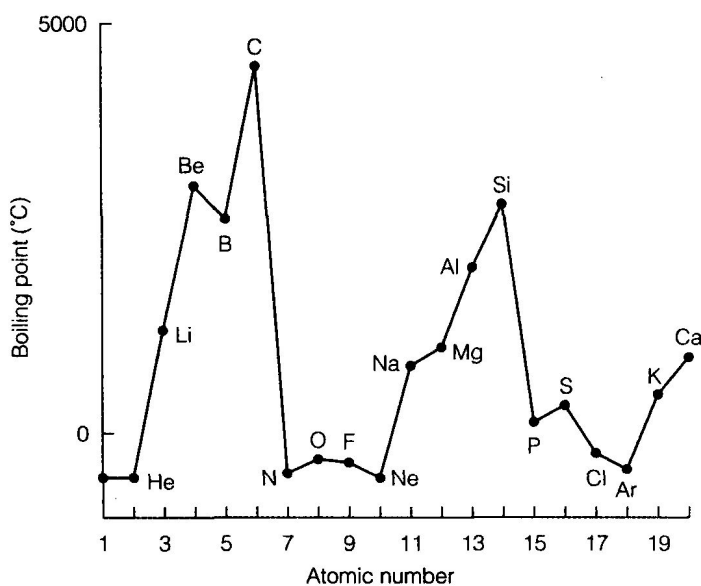


Fig. 2. Variation of boiling point with atomic number.