时代教育 • 国外高校优秀教材精选

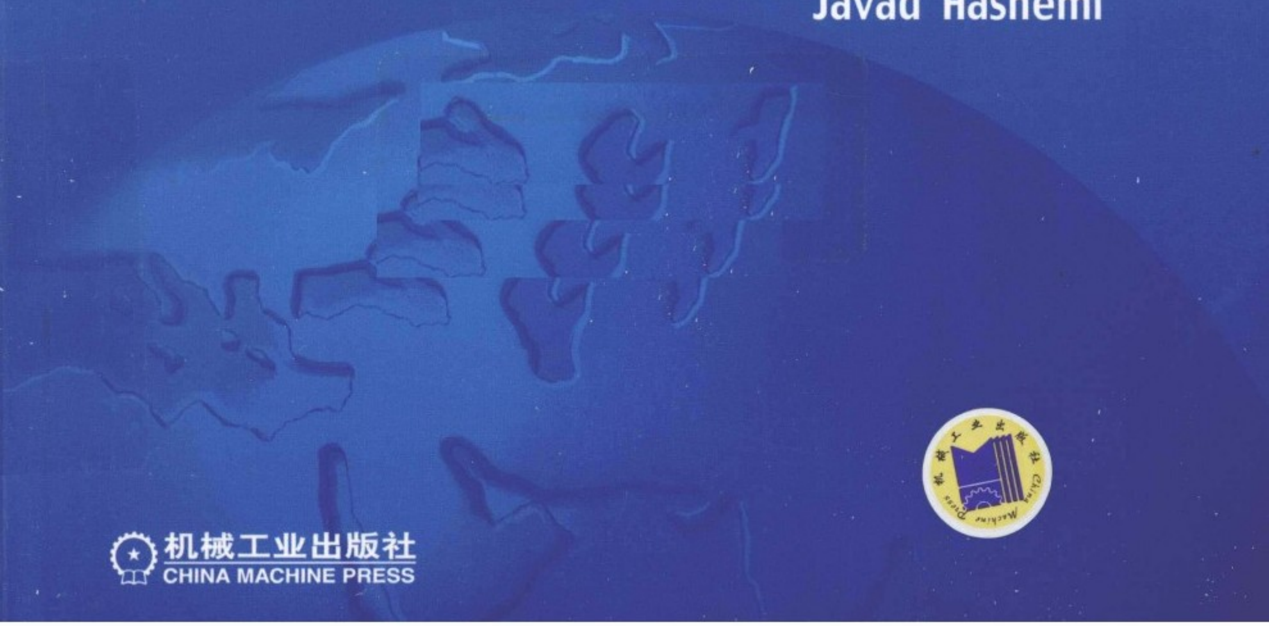
McGraw Hill Education

（英文版·原书第5版）

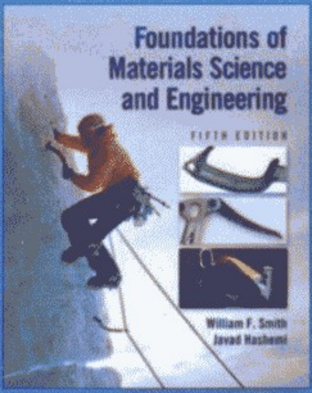
材料科学与工程基础

Foundations of Materials Science and Engineering

（美） William F. Smith
Javad Hashemi 著



机械工业出版社
CHINA MACHINE PRESS



Foundations of Materials Science and Engineering

FIFTH EDITION

William F. Smith

Javad Hashemi

本书在保持“以学生为朋友”的写作风格和密切联系工业应用的特色外，广泛引入现代材料科学的前沿课题，使学生开阔眼界，紧跟潮流，具有很好的时效性。

相对第4版，本书有如下改进：

1. 结合对原子结构、结合键及二者对材料性质和行为影响的最新理解，作者对原子结构和结合键部分进行了改写，使得内容更精确生动、更新颖。

2. 纳米技术的知识和应用也包括在各个相关章节中，包括纳米尺度特征材料的性能、研究纳米尺度特征所需的仪器以及制造技术等。

3. 对于每一章，都开发引入了新的问题，且属于综合和评价性问题，可以帮助教师更有效地训练学生，使其成为更富理解力的工程师和科学家。

4. 提供教师用的PPT教案，包含技术视频文件类、解题辅导以及虚拟的实验室实验，需填写教师反馈表向McGraw-Hill公司索取。另外该课程还有丰富的网上在线资源，详见www.mhhe.com/smithmaterials5。

This edition is authorized for sale in the People's Republic of China only, excluding Hong Kong, Macao SAR and Taiwan.
此英文影印删减版仅限在中华人民共和国境内（不包括中国香港、澳门特别行政区及中国台湾地区）销售。

ISBN 978-7-111-32461-4
策划编辑：冯春生、丁昕祯
封面设计：路恩中

上架指导：材料机械类

地址：北京市百万庄大街22号
电话服务
社服务中心：(010)88361066
销 售 一 部：(010)68326294
销 售 二 部：(010)88379649
读者服务部：(010)68993821

邮政编码：100037
网络服务
门户网：http://www.cmpbook.com
教材网：http://www.cmpedu.com
封面无防伪标均为盗版

定价：90.00元

ISBN 978-7-111-32461-4
9 787111 324614

时代教育·国外高校优秀教材精选

材料科学与工程基础

（英文版·原书第5版）

Foundations of Materials Science and Engineering

机械工业出版社

William F. Smith
Foundations of Materials Science and Engineering, 5e
978-0-07-352924-9
Copyright © 2010 by McGraw-Hill Companies, Inc.
All Rights reserved. No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including without limitation photocopying, recording, taping, or any database, information or retrieval system, without the prior written permission of the publisher.
This authorized English Abridgement edition is jointly published by McGraw-Hill Education (Asia) and China Machine Press. This edition is authorized for sale in the People's Republic of China only, excluding Hong Kong, Macao SAR and Taiwan.
Copyright © 2010 by McGraw-Hill Education (Asia), a division of the Singapore Branch of The McGraw-Hill Companies, Inc.

版权所有。未经出版人事先书面许可，对本出版物的任何部分不得以任何方式或途径复制或传播，包括但不限于复印、录制、录音，或通过任何数据库、信息或可检索的系统。

本授权英文删减影印版由麦格劳-希尔（亚洲）教育出版公司和机械工业出版社合作出版。此版本经授权仅限在中华人民共和国境内（不包括香港特别行政区、澳门特别行政区和台湾地区）销售。

版权© 2010 由麦格劳-希尔（亚洲）教育出版公司所有。

本书封面贴有 McGraw-Hill 公司防伪标签，无标签者不得销售。

北京市版权局著作权合同登记号：01-2010-3213

图书在版编目（CIP）数据

材料科学与工程基础：第5版：英文/（美）史密斯（Smith，W. F.），（美）哈希米（Hashemi，J.）著．—北京：机械工业出版社，2011.1
（时代教育·国外高校优秀教材精选）
ISBN 978-7-111-32461-4

Ⅰ.①材… Ⅱ.①史…②哈… Ⅲ.①材料科学—高等学校—教材—英文 Ⅳ.①TB3

中国版本图书馆 CIP 数据核字（2010）第234349号

机械工业出版社（北京市百万庄大街22号 邮政编码100037）
策划编辑：冯春生 丁昕祯 责任编辑：冯春生 丁昕祯
版式设计：霍永明 封面设计：路恩中
责任印制：乔 宇
三河市国英印务有限公司印刷
2011年1月第1版第1次印刷
184mm×260mm · 51.25印张 · 1300千字
标准书号：ISBN 978-7-111-32461-4
定价：90.00元

凡购本书，如有缺页、倒页、脱页，由本社发行部调换

电话服务	网络服务
社服务中心：(010)88361066	门户网：http://www.cmpbook.com
销售一部：(010)68326294	教材网：http://www.cmpedu.com
销售二部：(010)88379649	
读者服务部：(010)68993821	封面无防伪标均为盗版

国外高校优秀教材审定委员会

主任委员：

杨叔子

委员（按姓氏笔画为序）：

丁丽娟　王先逵　王大康　白峰衫　石德珂
史荣昌　田民波　孙洪祥　朱孝禄　陆启韶
张润琦　张　策　张三慧　张福润　张延华
吴宗泽　吴　麒　宋心琦　李俊峰　余远斌
陈文楷　陈立周　单辉祖　杨王玥　俞正光
赵汝嘉　郭可谦　翁海珊　龚光鲁　章栋恩
黄永畅　谭泽光　郭鸿志

出版说明

随着我国加入WTO，国际间的竞争越来越激烈，而国际间的竞争实际上也就是人才的竞争、教育的竞争。为了加快培养具有国际竞争力的高水平技术人才，加快我国教育改革的步伐，国家教育部出台了倡导高校开展双语教学、引进原版教材的政策。以此为契机，机械工业出版社陆续推出了一系列国外影印版教材，其内容涉及高等学校公共基础课，以及机、电、信息领域的专业基础课和专业课。

引进国外优秀原版教材，在有条件的学校推动开展英语授课或双语教学，自然也引进了先进的教学思想和教学方法，这对提高我国自编教材的水平，加强学生的英语实际应用能力，使我国的高等教育尽快与国际接轨，必将起到积极的推动作用。

为了做好教材的引进工作，机械工业出版社特别成立了由著名专家组成的国外高校优秀教材审定委员会。这些专家对实施双语教学做了深入细致的调查研究，对引进原版教材提出了许多建设性意见，并慎重地对每一本将要引进的原版教材一审再审，精选再精选，确认教材本身的质量水平，以及权威性和先进性，以期所引进的原版教材能适应我国学生的外语水平和学习特点。在引进工作中，审定委员会还结合我国高校教学课程体系的设置和要求，对原版教材的教学思想和方法的先进性、科学性严格把关。同时尽量考虑原版教材的系统性和经济性。

这套教材出版后，我们将根据各高校的双语教学计划，及时地将其推荐给各高校选用。希望高校师生在使用教材后及时反馈意见和建议，使我们更好地为教学改革服务。

机械工业出版社

第 5 版影印前言

由 William F. Smith 和 Javad Hashemi 编写的《材料科学与工程基础》（Foundations of Materials Science and Engineering）第 5 版于 2009 年由 Mc Graw-Hill，Inc. 出版。2006 年机械工业出版社曾影印出版该书的第 4 版。西安交通大学石德珂教授撰写了极富指导性的影印前言。石教授的观点对于第 5 版仍然适用，在此不再重复。

William F. Smith 是佛罗里达大学机械和航空航天工程系的工程学教授，曾在加利福尼亚州和佛罗里达州担任注册职业工程师，教授本科生和研究生的材料科学与工程课程，并长年不懈地积极从事教材的编写。作者的学识和经历，特别是注册职业工程师的实践经验，再加上教材的多次再版改进，保证了本书的水平和质量。

本书在保持“以学生为朋友”的写作风格和密切联系工业应用的特色之外，至始至终广泛引入现代材料科学的前沿课题，使学生开阔眼界，紧跟潮流。与第 4 版相比，本书在教授方式、习题编排、多媒体运用等方面都有较大的改进。

随着科学技术的进步、新工程领域的发展，以及工程专业的变化，今天的工程师必须在与材料相关的领域具备更深入、更广阔、更时新的知识。至少，所有工科大学生都必须掌握有关各类工程材料的结构、性能、加工、应用等方面的基础知识。这是在每天常规的工程实际中对材料做出正确选择的至关重要的一步。同样，对这些知识的更深入理解，对于复杂系统的设计者、事故（材料失效）的分析者、研发工程师和科学家都是必不可少的。

因此，为培养未来的材料工程师和科学家，《材料科学与工程基础》在兼顾适当的广度和深度两方面的前提下，力求呈现更加广泛的内容。本书在内容设置上照顾到材料科学概念（基础知识）和材料工程（应用知识）的相对均衡。基础和应用概念藉由多种环节和手段集中呈现在读者面前，其中包括：简明的课文解释、贴切而引人注目的图像、详尽的试样分析、电子辅助系统和课外作业等。因此，本教科书既适用于材料概论课程（大学二年级以前），又适用于更高年级（三、四年级）后续的材料科学与工程课程。最后需要指出的是，第 5 版及其辅助资源是按照满足不同学生的各种学习风格而设计的。众所周知，现在的大学生并非是按同一手段和借助同一种工具来学习的。

第 5 版的改进主要包括下述几个方面：

1. 关于原子结构和结合键的第 2 章被重新改写。新的描述建立在对原子结构、结合键及二者对材料性质和行为影响的最新理解的基础之上。其结果，内容更精确、更新颖。一些重要的改进包括：①对该领域的关键进展给出一个简明而有意思的历史透视，这会使教师和学生双方易于接受，②对多电子原子的结合键概念作了更详尽的讨论；③给出晶格能的概念；④对结合键类型与材料性能之间的关系作了更详尽的讨论；⑤增加了新的例题和课外作业。

2. 纳米技术的论题已包括在各个相关章节中。这些论题包括纳米尺度特征（例如，纳米晶粒尺寸）材料的研究，研究纳米尺度特征所需要的仪器、制造技术以及纳米尺度特征材料的性能等。

3. 每章后面的习题已由教师按照学生学习、理解的水平作了分类。分类是建立在 Bloom's 分类学的基础上，并力图帮助学生和教师实现教学计划所要求的目标和标准。分类的第一组习题是知识

性和理解性的问题。这些问题的回答要求学生掌握最基本的入门知识，包括内容的回忆及事实的识别等。向学生提出的大部分问题是要完成诸如定义、描述、罗列以及命名之类的回答。第二组是应用和分析类的问题。在这一组问题中，要求学生运用所学的知识解决某一问题，说明某一概念，并进行计算和分析。最后的第三组问题被称为综合性和评价性问题。在这一组问题中，要求学生以本章所学内容为基础，进行识别、评价、设计、估计、评定，并且综合为一般意义上的新的理解。值得注意的是，这类问题尽管不以难易程度为指标，但却能以简单的方式考查学生的理解与判别能力。

4. 对于每一章，都开发引入了新的问题，且大部分属于综合性和评价性问题。这些问题力图使学生以更深入和更全面的方式进行思考。这是作者的一个主要目标——帮助教师更有效地训练学生，使他们成为更富理解力的工程师和科学家。

5. 第5版的另一个令人振奋的新特点是附有教师用PPT教案。这些内容详尽、表述简洁的PPT教案是高度集成的结果，其中包括技术视频文件类、解题辅导以及虚拟的实验室试验。PPT教案是为满足不同的教学风格，包括革新型、解析型、常识介绍型和动态教学型等而设计的。这不仅为教师提供了一个强有力的演示工具，而且增加了学生学习这一课程的兴趣。作者强烈地推荐该课程的教师预先观看并亲手操作每一节课的PPT演示。这对于新教师来说可能是极有帮助的。

考虑到本书的大部分读者可能是第一次接触到材料科学，因此在内容编排上力求做到主题鲜明、叙述简练，尽量避免繁琐的内容，以免读者望而却步。遍布全书的工业应用实例和照片等向学生们表明，材料科学与工程无处不在地应用于现实世界中。

本书可作为材料科学与工程专业教材，也可作为机械、动力类专业相应课程的教学参考书。本书对各专业工程技术和科技人员也具有重要的参考价值。

田民波

于清华大学材料科学与工程系

第 4 版影印前言

材料科学是阐述材料的内部结构、性能和加工成形过程的基础知识；材料工程是应用这些基础知识使材料转化为社会所需的产品。材料科学与工程就是将两者结合起来、它是基础学科（物理、化学、力学、数学）和各种工程学科（机械、动力、能源、化工、航空等）之间的桥梁。

Smith 是一位有丰富教学经验的教授。他的著作《Structure and Properties of Engineering Alloys》(1981) 已于 1984 年由我国翻译出版。随后他又写了《Principles of Materials Science and Engineering》(1986)，在国内有影印本。这两本书当时受到了广泛关注，并对专业教学产生了一定影响。本书是作者在上述书的基础上扩充改写而成。

本书是材料科学与工程专业学生的第一门入门课，它要让初学者先对专业有一个概貌性的了解，并获得一定的基础知识和材料方面的知识。在过去的专业教学中，“材料科学基础”和“材料学”是分课设置，各按学科自成体系。学生在学习过程中；常感“材料科学基础”抽象难学，不知学有何用，而对后续课“材料学”又感到繁琐枯燥，缺少理论依托，因而也未能真正理解消化。本书克服了这一缺憾，将材料科学基础与材料学两者有机地结合起来，以材料为中心，从培养材料工程师着眼，有选择地选取基础知识内容，将本书化解为四个交叉组成部分：①基础知识；②材料制备方法；③各种材料；④材料的力学、物理和化学性能。这种组合方式的优点是结构紧凑，内容精炼，完整实用，学生受益。例如，第 13 章腐蚀，如有该章做基础，似乎不必另开一门“金属的腐蚀和防护”，有了第 14、15、16 章的基础知识，似乎也不必另开一门“材料物理性能”来讨论电、磁、光、超导等，而这些知识又和具体材料结合起来，突显出学以致用。值得注意的是，在美国似乎现已趋于这种教学体系。

本书的另一突出优点是在每章之后都贯穿有材料选择与设计的专门思考题，这是作者精心设计的，也是他多年教学经验的积累。每个题目都是从工程实际出发，科学地培养学生的研究方法和分析思路，能真正使学生在正确选材的能力上有所提高，也为开发创新材料打下良好的基础。这里我们可略举一些例子。例如，第 2 章原子结构与结合键中的思考题：石墨和金刚石都是由碳原子构成，为什么在性能上有如此大的差异？不锈钢中含有大量铬，为什么铬能防止腐蚀？第 3 章晶体结构中的习题：给你一未知材料，你能用哪些方法识别它？通常，在高温高应力下工作的燃气轮机叶片，制备成大的单晶，你认为单晶叶片有什么优点？应选取什么材料？（虽然学生暂时不能给予这几个问题全面正确的答案，但对培养同学思考和下一章的深入学习有帮助。）在第 4 章凝固、晶体缺陷和扩散中的习题：燃气轮机叶片由长的柱状晶组成，试提出实现方向性凝固的方法；从凝固观点解释焊接过程，影响焊接接头的关键因素有哪些？两种不同的金属接触，会产生柯肯达尔效应，如何解释这一现象？需要指出的是，这几道习题原本是传统教材中的讲课内容，现延伸为本章的课外作业，在启发学生思考，指导学生自学以后，同样获得了上述知识，显然这种学习方法印象更深，兴趣更大。又如第 12 章复合材料中的习题：用纤维可增加陶瓷材料的韧性，但在这种情况下，纤维与基体的结合应不是很强，试解释这个过程何以能韧化陶瓷材料？该题点出了韧化陶瓷材料的技术关键。本书每章的最后都落脚于材料的选择与设计，在培养学生这方面的能力上，可谓用心良苦。

除了上述两个特点外，该书在内容上也有许多可圈可点之处。例如，在第2章的结合键中对过渡金属和陶瓷材料的混合键有清楚的分析；在第3章晶体结构中，对晶面指数和方向指数的表示作了极详尽的说明，这虽看似简单，但在教学上体会到必须做大量练习才能使学生牢固掌握。特别地，全书自始至终广泛引入现代材料科学的前沿课题，如对智能材料器件、MEMs、纳米材料、超级合金及其在生物医学应用方面等的首次介绍，使学生能够开阔眼界，紧跟潮流；大量精美的插图，强化了相关的内容，尤其是每章均引入压题照片，处处向学生表明材料科学与工程无处不在地应用于现实世界中。

本书可作为材料科学与工程专业教材，也可作为机械、动力类专业相应课程的教学参考书；对材料工程师和科技人员，也是一本有用的工具书。

石德珂

于西安交通大学

ABOUT THE AUTHORS

Javad Hashemi is a Professor of Mechanical Engineering at Texas Tech University and is currently serving as the Associate Dean for Research in the Edward E. Whitacre College of Engineering. Javad received his Ph.D. in Mechanical Engineering from Drexel University in 1988. He has been teaching undergraduate and graduate materials and mechanics courses, as well as laboratories, at Texas Tech University since 1991. Dr. Hashemi has an extensive research background in manufacturing, structural, and synthesis aspects of materials. His current research focus is the areas of materials, biomaterials, and engineering education.

The late **William F. Smith** was Professor Emeritus of Engineering in the Mechanical and Aerospace Engineering Department of the University of Central Florida at Orlando, Florida. He was awarded an M.S. degree in metallurgical engineering from Purdue University and a Sc.D. degree in metallurgy from Massachusetts Institute of Technology. Dr. Smith, who was a registered professional engineer in the states of California and Florida, taught undergraduate and graduate materials science and engineering courses and actively wrote textbooks for many years. He was also the author of *Structure and Properties of Engineering Alloys,* Second Edition (McGraw-Hill, 1993).

PREFACE

The subject of materials science and engineering is an essential course to engineers and scientists from all disciplines. With advances in science and technology, development of new engineering fields, and changes in the engineering profession, today's engineer must have a deeper, more diverse, and up-to-date knowledge of materials-related issues. At a minimum, all engineering students must have the basic knowledge of the structure, properties, processing, and performance of various classes of engineering materials. This is a crucial first step in the materials selection decisions in every day rudimentary engineering problems. A more in-depth understanding of the same topics is necessary for designers of complex systems, forensic (materials failure) analysts, and research and development engineers/scientists.

Accordingly, to prepare materials engineers and scientists of the future, *Foundations of Materials Science and Engineering* is designed to present diverse topics in the field with both appropriate breadth and depth. The strength of the book is in its balanced presentation of concepts in science of materials (basic knowledge) and engineering of materials (applied knowledge). The basic and applied concepts are integrated through concise textual explanations, relevant and stimulating imagery, detailed sample problems, electronic supplements, and homework problems. This textbook is therefore suitable for both an introductory course in materials at the sophomore level and a more advanced (junior/senior level) second course in materials science and engineering. Finally, the fifth edition and its supporting resources are designed to address a variety of student learning styles based on the well-known belief that not all students learn in the same manner and with the same tools.

The following improvements have been made to the fifth edition:

- The chapter on atomic structure and bonding, Chapter 2, has been rewritten. The new presentation is based on the more recent understandings of the atomic structure, bonding, and their influence on material properties and behavior. As a result, the coverage is more accurate and up-to-date. Important improvements include: (1) a concise and interesting historical perspective on the key advances in the field that we are sure both the instructors and the students will enjoy and appreciate; (2) the concept of bonding in multi-electron atoms is discussed in more detail; (3) the concept of lattice energy is presented; (4) the relationship between type of bonding and material properties is explained in more detail; and (5) new example and homework materials to support the other changes.
- Nanotechnology topics have been included in various related chapters. These topics include the study of materials with nano-scale features (for instance, nano grain size), instruments that are needed to study nano-scale features, processing techniques, and properties of materials with nano-scale features.

- The ever growing and changing field of biomedical engineering inspired the addition of a new chapter on biomaterials (Chapter 17). The main topics of the chapter include a discussion of the behavior of structural materials (metals, ceramics, polymers, and composites) inside the human body in orthopedic applications and biocompatibility issues and a discussion of the structure, properties, and behavior of biological materials (including bone, ligaments and cartilage). We introduce biological materials because they are the state of the art in smart materials with nano-scale features.
- The end-of-chapter problems have been classified according to the learning/understanding level expected from the student by the instructor. The classification is based on Bloom's Taxonomy and is intended to help students as well as instructors to set goals and standards for learning objectives. The first group in the classification is the Knowledge and Comprehension Problems. These problems will require students to show learning at the most basic level of recall of information and recognition of facts. Most problems ask the students to perform tasks such as define, describe, list, and name. The second group is the Application and Analysis Problems. In this group, students are required to apply the learned knowledge to the solution of a problem, demonstrate a concept, calculate, and analyze. Finally, the third class of problems is called Synthesis and Evaluation Problems. In this class of problems, the students are required to judge, evaluate, design, develop, estimate, assess, and in general synthesize new understanding based on what they have learned from the chapter. It is worth noting that this classification is not indicative of the level of difficulty, but simply different cognitive levels.
- For each chapter, new problems—mostly in the synthesis and evaluation category—have been developed. These problems are intended to make the students think in a more in-depth and reflective manner. This is an important objective of the authors to help the instructors train engineers and scientists that operate at a higher cognitive domain.
- Another exciting new feature of the fifth edition is the instructors' PowerPoint® lectures. These detailed, yet succinct, PowerPoint lectures are highly interactive and contain technical video clips, tutorials for problem solving, and virtual laboratory experiments. The PowerPoint lectures are designed to address a variety of learning styles including innovative, analytic, common sense, and dynamic learners. Not only is this a great presentation tool for the instructor, it creates interest in the student to learn the subject more effectively. We strongly recommend that the instructors for this course view and test these PowerPoint lecture presentations. This could especially be helpful for new instructors.

Online Resources

The text website contains a variety of resources for students and instructors at www.mhhe.com/smithmaterials5. Materials for students include:

Three virtual labs with video, interactive quizzing, and step-by-step, real-life processes; a lab manual that coordinates with the virtual labs; MatVis crystal visualization software so students can create crystal structures as well as view existing structures; animations; a searchable materials properties database.

Materials for instructors include: lecture PowerPoint slides with animations, videos, and images not in the text; a solutions manual; teaching resources to help instructors incorporate the virtual labs and other media into class; text images; and sample syllabi.

Electronic Textbook Options

Ebooks are an innovative way for students to save money and create a greener environment at the same time. An ebook can save students about half the cost of a traditional textbook and offers unique features like a powerful search engine, highlighting, and the ability to share notes with classmates using ebooks.

McGraw-Hill offers two ebook options: purchasing a downloadable book from VitalSource or a subscription to the book from CourseSmart. To talk about the ebook options, contact your McGraw-Hill sales rep or visit the sites directly at www.vitalsource.com and www.coursesmart.com.

ACKNOWLEDGMENTS

The co-author, Javad Hashemi, would like to dedicate his efforts on this textbook to the eternal-loving memory of his parents Seyed-Hashem and Sedigheh; to his wife, mentor, and friend, Eva; to his sons Evan Darius and Jonathon Cyrus; and last but not least to his siblings (thank you for your ceaseless love and support).

The authors would like to acknowledge the efforts of the collaborating author, Dr. Naveen Chandrashekar, Assistant Professor of Mechanical Engineering at University of Waterloo for writing the sections on biological materials and assembling the chapter, developing the PowerPoint® slides, the table of properties, and assisting with the development of virtual labs and tutorials. The authors would also like to acknowledge the support of Allen Conway and Metallurgical Technologies Inc., for giving us access to their case studies and images. We sincerely appreciate their help. Finally, we appreciate and acknowledge the efforts of Dr. Greg I. Gellene, Professor of Chemistry, Texas Tech University for reading the Chapter on Chemistry and providing his invaluable input.

The authors would like to acknowledge with appreciation the numerous and valuable comments, suggestions, constructive criticisms, and praise from the following evaluators and reviewers:

Betty Lise Anderson, *Ohio State University*
Behzad Bavarian, *California State University—Northridge*
William Brower, *Marquette University*
Charles M. Gilmore, *George Washington Univrsity*
Brian Grady, *University of Oklahoma*
Mamoun Medraj, *Concordia University*
David Niebuhr, *California Polytechnic State University*
Dr. Devesh Misra, *University of Louisiana at Lafayette*
Halina Opyrchal, *New Jersey Institute of Technology*
John R. Schlup, *Kansas State University*
Raymond A. Fournelle, *Marquette University*

Javad Hashemi

目　　录

出版说明

第 5 版影印前言

第 4 版影印前言

Perface

第 1 章　材料科学与工程引论 …………………… 2
1.1　材料与工程 ……………………………………… 3
1.2　材料科学与工程 ………………………………… 6
1.3　材料的种类 ……………………………………… 8
1.3.1　金属材料 ……………………………………… 8
1.3.2　聚合物材料 …………………………………… 10
1.3.3　陶瓷材料 ……………………………………… 11
1.3.4　复合材料 ……………………………………… 13
1.3.5　电子材料 ……………………………………… 14
1.4　材料间的竞争 …………………………………… 15
1.5　材料科学与技术的最新进展和未来趋势 …… 17
1.5.1　智能材料 ……………………………………… 17
1.5.2　纳米材料 ……………………………………… 19
1.6　材料设计与选择 ………………………………… 19
1.7　第 1 章小结 ……………………………………… 20
1.8　定义 ……………………………………………… 21
1.9　习题 ……………………………………………… 22
第 2 章　原子结构与键合 ………………………… 24
2.1　原子结构和亚原子粒子 ………………………… 25
2.2　原子序数、质量数和相对原子质量 ………… 28
2.3　原子的电子结构 ………………………………… 31
2.3.1　普朗克量子理论和电磁辐射 ………………… 31
2.3.2　氢原子的玻尔理论 …………………………… 34
2.3.3　不确定原理和薛定谔波函数 ………………… 37
2.3.4　量子数、能级和原子轨道 …………………… 40
2.3.5　多电子原子的能态 …………………………… 43
2.3.6　量子力学模型和元素周期表 ………………… 44
2.4　原子尺寸、离化能和电子亲合力的周期性变化 …… 49
2.4.1　原子尺寸的变化趋势 ………………………… 49
2.4.2　离化能的变化趋势 …………………………… 49
2.4.3　电子亲和力的变化趋势 ……………………… 52
2.4.4　金属、类金属和非金属 ……………………… 52
2.5　一次键 …………………………………………… 54
2.5.1　离子键 ………………………………………… 55
2.5.2　共价键 ………………………………………… 61
2.5.3　金属键 ………………………………………… 68
2.5.4　混合键 ………………………………………… 70
2.6　二次键 …………………………………………… 71
2.7　第 2 章小结 ……………………………………… 74
2.8　定义 ……………………………………………… 75
2.9　习题 ……………………………………………… 77
第 3 章　材料中的晶体结构和非晶态结构 … 84
3.1　空间点阵和晶胞 ………………………………… 85
3.2　晶系与布拉菲点阵 ……………………………… 86
3.3　主要的金属晶体结构 …………………………… 87
3.3.1　体心立方（BCC）晶体结构 ………………… 89
3.3.2　面心立方（FCC）晶体结构 ………………… 92
3.3.3　密排六方（HCP）晶体结构 ………………… 93
3.4　立方晶胞中的原子位置 ………………………… 95
3.5　立方晶胞中的晶向 ……………………………… 96
3.6　立方晶胞中晶面的米勒指数 ………………… 100
3.7　密排六方晶体结构中的晶面和晶向 ………… 105
3.7.1　HCP 晶胞中的晶面指数 …………………… 105
3.7.2　HCP 晶胞中的晶向指数 …………………… 106
3.8　FCC、HCP 和 BCC 晶体结构的比较 ……… 108
3.8.1　FCC 和 HCP 晶体结构 ……………………… 108
3.8.2　BCC 晶体结构 ………………………………… 110
3.9　体密度、面密度以及线密度的晶胞计算 … 110
3.9.1　体密度 ………………………………………… 110
3.9.2　面密度 ………………………………………… 111
3.9.3　线密度 ………………………………………… 113
3.10　多晶型或同素异构 …………………………… 114
3.11　晶体结构分析 ………………………………… 115
3.11.1　X 光源 ……………………………………… 116

3.11.2　X光衍射 …… 117
3.11.3　晶体结构的X光衍射分析 …… 119
3.12　非晶态材料 …… 125
3.13　第3章小结 …… 126
3.14　定义 …… 127
3.15　习题 …… 128
第4章　凝固和晶体缺陷 …… 136
4.1　金属的凝固 …… 137
4.1.1　液态金属中稳定晶核的形成 …… 139
4.1.2　液态金属中晶体生长与晶粒结构的形成 …… 144
4.1.3　工业铸件中的晶粒结构 …… 145
4.2　单晶体的凝固 …… 146
4.3　金属固溶体 …… 150
4.3.1　置换式固溶体 …… 151
4.3.2　间隙式固溶体 …… 153
4.4　晶体缺陷 …… 155
4.4.1　点缺陷 …… 155
4.4.2　线缺陷（位错） …… 156
4.4.3　面缺陷 …… 159
4.4.4　体缺陷 …… 162
4.5　鉴别微观结构和缺陷的实验技术 …… 163
4.5.1　光学金相、ASTM晶粒尺寸和晶粒直径的确定 …… 163
4.5.2　扫描电子显微镜（SEM） …… 168
4.5.3　透射电子显微镜（TEM） …… 169
4.5.4　高分辨率透射电子显微镜（HRTEM） …… 170
4.4.5　扫描探针显微镜和原子分辨率 …… 173
4.6　第4章小结 …… 176
4.7　定义 …… 177
4.8　习题 …… 178
第5章　热激活过程和固体中的扩散 …… 186
5.1　固体中的速率过程 …… 187
5.2　固体中的原子扩散 …… 191
5.2.1　固体中的扩散概述 …… 191
5.2.2　扩散机制 …… 191
5.2.3　稳态扩散 …… 193
5.2.4　非稳态扩散 …… 196
5.3　扩散过程的工业应用 …… 198
5.3.1　气体渗碳使钢铁表面硬化 …… 198
5.3.2　集成电路用硅晶圆的杂质扩散 …… 202
5.4　温度对固体扩散的影响 …… 204
5.5　第5章小结 …… 208
5.6　定义 …… 208
5.7　习题 …… 209
第6章　金属的力学性能（Ⅰ） …… 214
6.1　金属与合金的成形加工 …… 215
6.1.1　金属和合金的铸造 …… 215
6.1.2　金属和合金的热轧和冷轧 …… 217
6.1.3　金属和合金的挤压 …… 221
6.1.4　锻造 …… 222
6.1.5　其他的金属成形工艺 …… 224
6.2　金属材料中的应力和应变 …… 225
6.2.1　弹性变形和塑性变形 …… 225
6.2.2　工程应力和工程应变 …… 226
6.2.3　泊松比 …… 228
6.2.4　切应力与切应变 …… 228
6.3　拉伸试验和工程应力-应变图 …… 230
6.3.1　由拉伸试验和工程应力-应变图获得的力学性能数据 …… 232
6.3.2　部分合金的工程应力-应变曲线的比较 …… 237
6.3.3 真应力和真应变 …… 237
6.4　硬度与硬度测试 …… 239
6.5　金属单晶体的塑性形变 …… 240
6.5.1　金属晶体表面的滑移带与滑移线 …… 240
6.5.2　金属晶体由滑移机制造成的塑性形变 …… 242
6.5.3　滑移系统 …… 244
6.5.4　金属单晶体的临界切应力 …… 249
6.5.5　施密特定律 …… 250
6.5.6　孪生 …… 252
6.6　多晶金属的塑性形变 …… 254
6.6.1　晶界对金属强度的影响 …… 254
6.6.2　塑性形变对晶粒形状和位错分布的影响 …… 256
6.6.3　冷塑性形变对金属强度增加的影响 …… 258
6.7　金属的固溶强化 …… 259
6.8　塑性形变金属的回复和再结晶 …… 261

6.8.1　深冷加工金属再加热之前的结构 …… 262
6.8.2　回复 …… 263
6.8.3　再结晶 …… 264
6.9　金属中的超塑性 …… 268
6.10　纳米晶金属 …… 270
6.11　第 6 章小结 …… 271
6.12　定义 …… 272
6.13　习题 …… 273
第 7 章　金属的力学性能（Ⅱ） …… 280
7.1　金属的断裂 …… 281
7.1.1　韧性断裂 …… 282
7.1.2　脆性断裂 …… 283
7.1.3　韧度和冲击试验 …… 286
7.1.4　韧性-脆性转变温度 …… 286
7.1.5　断裂韧度 …… 289
7.2　金属的疲劳 …… 291
7.2.1　周期应力 …… 295
7.2.2　韧性金属在疲劳过程中发生的基本结构变化 …… 296
7.2.3　影响金属疲劳强度的几个主要因素 …… 297
7.3　疲劳裂纹扩展速率 …… 298
7.3.1　疲劳裂纹扩展与应力、裂纹长度的关系 …… 298
7.3.2　疲劳裂纹扩展速率与应力强度因子范围作图 …… 300
7.3.3　疲劳寿命计算 …… 302
7.4　金属的蠕变和应力断裂 …… 304
7.4.1　金属的蠕变 …… 304
7.4.2　蠕变试验 …… 306
7.4.3　蠕变-断裂试验 …… 307
7.5　第 7 章小结 …… 308
7.6　定义 …… 309
7.7　习题 …… 309
第 8 章　相图 …… 316
8.1　纯物质的相图 …… 317
8.2　吉布斯相律 …… 319
8.3　冷却曲线 …… 320
8.4　二元匀晶合金系统 …… 321
8.5　杠杆定律 …… 324
8.6　合金的非平衡凝固 …… 328
8.7　二元共晶合金系统 …… 331
8.8　二元包晶合金系统 …… 339
8.9　二元偏晶系统 …… 344
8.10　不变反应 …… 345
8.11　有中间相和中间化合物的相图 …… 347
8.12　三元相图 …… 351
8.13　第 8 章小结 …… 354
8.14　定义 …… 355
8.15　习题 …… 357
第 9 章　工程合金 …… 366
9.1　铁和钢的生产 …… 368
9.1.1　高炉中的生铁生产 …… 368
9.1.2　炼钢和主要钢铁产品形式的加工 …… 369
9.2　铁-碳系统 …… 371
9.2.1　铁-铁-碳化物相图 …… 371
9.2.2　Fe-Fe$_3$C 相图中的固相 …… 371
9.2.3　Fe-Fe$_3$C 相图中的不变反应 …… 372
9.2.4　碳素钢的缓慢冷却 …… 374
9.3　普通碳素钢的热处理 …… 381
9.3.1　马氏体 …… 381
9.3.2　奥氏体的等温分解 …… 386
9.3.3　共析碳素钢的连续冷却转变曲线 …… 391
9.3.4　碳素钢的退火与正火 …… 394
9.3.5　碳素钢的回火 …… 395
9.3.6　碳素钢的分类与典型的力学性能 …… 399
9.4　低合金钢 …… 400
9.4.1　合金钢的分类 …… 400
9.4.2　合金钢中合金元素的分布 …… 402
9.4.3　合金元素对钢的共析温度影响 …… 403
9.4.4　淬硬性 …… 404
9.4.5　低合金钢典型的力学性能和应用 …… 409
9.5　铝合金 …… 409
9.5.1　析出强化（硬化） …… 411
9.5.2　铝及其产品的一般性能 …… 418
9.5.3　锻造铝合金 …… 419
9.5.4　铸造铝合金 …… 424
9.6　第 9 章小结 …… 426
9.7　定义 …… 427
9.8　习题 …… 428

第 10 章 聚合物材料 …… 436
10.1 概述 …… 437
10.1.1 热塑性塑料 …… 438
10.1.2 热固性塑料 …… 438
10.2 聚合反应 …… 439
10.2.1 单个乙烯分子的共价键结构 …… 439
10.2.2 一个活化乙烯分子的共价键结构 …… 440
10.2.3 聚乙烯聚合的整体反应和聚合度 …… 441
10.2.4 链式聚合步骤 …… 441
10.2.5 热塑性塑料的平均相对分子质量 …… 443
10.2.6 单体的官能度 …… 444
10.2.7 非晶体线性聚合物的结构 …… 444
10.2.8 乙烯基树脂与亚乙烯基树脂 …… 446
10.2.9 均聚物与共聚物 …… 447
10.2.10 其他聚合方法 …… 450
10.3 工业用聚合方法 …… 452
10.4 一些热塑性塑料的结晶度与立体异构现象 …… 454
10.4.1 非晶态热塑性塑料的凝固 …… 454
10.4.2 半晶态热塑性塑料的凝固 …… 454
10.4.3 半晶态热塑性塑料的结构 …… 456
10.4.4 热塑性塑料的立体异构现象 …… 457
10.4.5 齐格勒（Ziegler）催化剂与纳塔（Natta）催化剂 …… 458
10.5 塑料的加工 …… 459
10.5.1 用于热塑性塑料的加工工艺 …… 460
10.5.2 用于热固性塑料的加工工艺 …… 464
10.6 通用热塑性塑料 …… 466
10.6.1 聚乙烯 …… 468
10.6.2 聚氯乙烯均聚物与共聚物 …… 471
10.6.3 聚丙乙烯 …… 473
10.6.4 聚苯乙烯 …… 473
10.6.5 聚丙烯腈 …… 474
10.6.6 苯乙烯丙烯腈（SAN） …… 475
10.6.7 ABS …… 475
10.6.8 聚甲基丙烯酸甲酯（PMMA） …… 477
10.6.9 氟塑料 …… 478
10.7 工程热塑性塑料 …… 479
10.7.1 聚酰胺（尼龙） …… 480
10.7.2 聚碳酸酯 …… 483
10.7.3 苯氧基树脂 …… 484
10.7.4 聚甲醛 …… 485
10.7.5 热塑性聚酯 …… 486
10.7.6 聚苯硫醚 …… 487
10.7.7 聚醚酰亚胺 …… 488
10.7.8 聚合物合金 …… 488
10.8 热固性塑料（热固性树脂） …… 489
10.8.1 酚醛塑料 …… 491
10.8.2 环氧树脂 …… 492
10.8.3 不饱和聚酯 …… 494
10.8.4 氨基树脂（尿素塑料和三聚氰胺） …… 495
10.9 第 10 章小结 …… 497
10.10 定义 …… 498
10.11 习题 …… 500
第 11 章 陶瓷材料 …… 510
11.1 概述 …… 511
11.2 简单陶瓷的晶体结构 …… 513
11.2.1 简单陶瓷化合物中的离子键和共价键 …… 513
11.2.2 存在于离子键固体中的简单离子排列 …… 514
11.2.3 氯化铯晶体（CsCl）结构 …… 517
11.2.4 氯化钠晶体（NaCl）结构 …… 518
11.2.5 FCC 与 HCP 晶格中的间隙位置 …… 522
11.2.6 闪锌矿晶体（ZnS）结构 …… 524
11.2.7 氟石晶体（CaF_2）结构 …… 526
11.2.8 反氟石晶体结构 …… 528
11.2.9 刚玉晶体（Al_2O_3）结构 …… 528
11.2.10 尖晶石（$MgAl_2O_4$）晶体结构 …… 528
11.2.11 钙钛矿（$CaTiO_3$）晶体结构 …… 528
11.2.12 碳和它的同素异形体 …… 529
11.3 硅酸盐结构 …… 533
11.3.1 硅酸盐结构的基本结构单元 …… 533
11.3.2 硅酸盐的岛状结构、链状结构及环状结构 …… 533
11.3.3 硅酸盐的片状结构 …… 533
11.3.4 硅酸盐的网络结构 …… 535
11.4 陶瓷制备过程 …… 536
11.4.1 材料准备 …… 537
11.4.2 成形 …… 537
11.4.3 热处理 …… 542

11.5 传统陶瓷和工程陶瓷 …… 544
  11.5.1 传统陶瓷 …… 544
  11.5.2 工程陶瓷 …… 547
11.6 陶瓷的力学性能 …… 549
  11.6.1 概述 …… 549
  11.6.2 陶瓷材料变形的机制 …… 549
  11.6.3 影响陶瓷材料强度的因素 …… 550
  11.6.4 陶瓷材料的韧度 …… 551
  11.6.5 部分稳定氧化锆（PSZ）的相变增韧 …… 553
  11.6.6 陶瓷的疲劳失效 …… 553
  11.6.7 陶瓷研磨剂材料 …… 555
11.7 陶瓷材料的热学性能 …… 556
  11.7.1 陶瓷耐火材料 …… 557
  11.7.2 酸性耐火材料 …… 558
  11.7.3 碱性耐火材料 …… 558
  11.7.4 航天航空器用陶瓷瓦绝热片 …… 558
11.8 玻璃 …… 558
  11.8.1 玻璃的定义 …… 560
  11.8.2 玻璃的转变温度 …… 560
  11.8.3 玻璃的结构 …… 561
  11.8.4 玻璃的组成 …… 562
  11.8.5 玻璃的粘性变形 …… 564
  11.8.6 玻璃的形成方法 …… 566
  11.8.7 钢化玻璃 …… 568
  11.8.8 化学强化玻璃 …… 568
11.9 陶瓷涂层和表面工程 …… 570
  11.9.1 硅酸盐玻璃涂层 …… 570
  11.9.2 氧化物和碳化物涂层 …… 570
11.10 纳米技术和陶瓷 …… 571
11.11 第11章小结 …… 573
11.12 定义 …… 574
11.13 习题 …… 575

第12章 复合材料 …… 582
12.1 概述 …… 583
12.2 增强塑料类复合材料用纤维 …… 584
  12.2.1 增强塑料用玻璃纤维 …… 584
  12.2.2 增强塑料用碳纤维 …… 587
  12.2.3 增强塑料用的芳族聚酰胺纤维 …… 589
  12.2.4 增强塑料类复合材料用的碳纤维、芳族聚酰胺纤维和玻璃纤维的力学性能比较 …… 589
12.3 纤维增强塑料类复合材料 …… 591
  12.3.1 纤维增强塑料的基体材料 …… 591
  12.3.2 纤维增强塑料 …… 592
  12.3.3 在等应变、等应力情况下的片状连续纤维塑料基体复合材料的弹性模量方程 …… 596
12.4 纤维增强塑料的开式模塑加工工艺 …… 601
  12.4.1 手铺成型工艺 …… 601
  12.4.2 喷射铺展成型工艺 …… 601
  12.4.3 真空包热压成型工艺 …… 602
  12.4.4 绕丝成型工艺 …… 603
12.5 纤维增强塑料的闭式模塑加工工艺 …… 604
  12.5.1 压塑与注射成型加工工艺 …… 604
  12.5.2 片状模塑复合材料（SMC）加工工艺 …… 605
  12.5.3 连续挤压成型加工工艺 …… 606
12.6 金属基和陶瓷基复合材料 …… 606
  12.6.1 金属基复合材料（MMCs） …… 606
  12.6.2 陶瓷基复合材料（CMCs） …… 608
12.7 第12章小结 …… 613
12.8 定义 …… 614
12.9 习题 …… 616

第13章 材料的电学性能 …… 624
13.1 金属的电导 …… 625
  13.1.1 金属电导现象的经典模型 …… 625
  13.1.2 欧姆定律 …… 627
  13.1.3 金属导体中电子的漂移速度 …… 631
  13.1.4 金属的电阻率 …… 632
13.2 电导性的能带模型 …… 636
  13.2.1 金属的能带模型 …… 636
  13.2.2 绝缘体的能带模型 …… 638
13.3 本征半导体 …… 638
  13.3.1 本征半导体的电导机制 …… 638
  13.3.2 纯硅晶体点阵中的电荷输运 …… 639
  13.3.3 元素本征半导体的能带图 …… 640
  13.3.4 元素本征半导体电导的定量关系 …… 641
  13.3.5 温度对本征半导体的影响 …… 643
13.4 非本征半导体 …… 645
  13.4.1 n型（负型）非本征半导体 …… 645
  13.4.2 p型（正型）非本征半导体 …… 647
  13.4.3 非本征硅半导体材料的掺杂剂 …… 649

13.4.4 掺杂剂对非本征半导体中的载流子浓度的影响 …… 649
13.4.5 在室温条件下总电离杂质浓度对硅中载流子迁移率的影响 …… 652
13.4.6 温度对非本征半导体电导率的影响 …… 653
13.5 半导体器件 …… 655
13.5.1 pn 结 …… 656
13.5.2 pn 结型二极管的一些应用 …… 659
13.5.3 双极性结型晶体管 …… 660
13.6 微电子学 …… 662
13.6.1 微电子平面双极性晶体管 …… 662
13.6.2 微电子平面场效应晶体管 …… 663
13.6.3 微电子集成电路的制作 …… 666
13.7 化合物半导体 …… 673
13.8 陶瓷的电学性能 …… 676
13.8.1 介电体的基本特性 …… 676
13.8.2 陶瓷绝缘体材料 …… 678
13.8.3 陶瓷电容器材料 …… 679
13.8.4 陶瓷半导体 …… 680
13.8.5 铁电陶瓷 …… 682
13.9 纳电子学 …… 685
13.10 第 13 章小结 …… 686
13.11 定义 …… 687
13.12 习题 …… 690

第 14 章 光学性质与超导材料 …… 696
14.1 概述 …… 697
14.2 光谱和电磁波频谱 …… 697
14.3 光的折射 …… 699
14.3.1 折射率 …… 699
14.3.2 光折射的斯涅耳定律 …… 701
14.4 光的吸收、辐射和反射 …… 702
14.4.1 金属 …… 702
14.4.2 硅酸盐玻璃 …… 703
14.4.3 塑料 …… 704
14.4.4 半导体 …… 706
14.5 发光 …… 707
14.5.1 光致发光 …… 708
14.5.2 阴极发光 …… 708
14.6 射线的受激发射和激光 …… 710
14.7 光导纤维 …… 714
14.7.1 光导纤维中的光损失 …… 714
14.7.2 单模和多模光导纤维 …… 715
14.7.3 光导纤维的加工 …… 716
14.7.4 现代光导纤维通信系统 …… 718
14.8 超导材料 …… 719
14.8.1 超导态 …… 719
14.8.2 超导体的磁学性质 …… 720
14.8.3 超导体中的电流和磁场 …… 722
14.8.4 高电流、高磁场超导体 …… 723
14.8.5 高临界温度（T_c）超导氧化物 …… 725
14.9 定义 …… 727
14.10 习题 …… 728

第 15 章 磁学性能 …… 732
15.1 概述 …… 733
15.2 磁场和参量 …… 733
15.2.1 磁场 …… 733
15.2.2 磁感应 …… 736
15.2.3 磁导率 …… 736
15.2.4 磁化率 …… 738
15.3 磁性的类型 …… 738
15.3.1 反磁性 …… 739
15.3.2 顺磁性 …… 739
15.3.3 铁磁性 …… 739
15.3.4 原子的单个未成对电子的磁矩 …… 741
15.3.5 反铁磁性 …… 743
15.3.6 亚铁磁性 …… 743
15.4 温度对铁磁性的影响 …… 743
15.5 铁磁畴 …… 744
15.6 决定铁磁畴结构的能量类型 …… 746
15.6.1 交换能量 …… 746
15.6.2 静磁能量 …… 747
15.6.3 磁晶各向异性能 …… 747
15.6.4 畴壁能量 …… 748
15.6.5 磁致伸缩能量 …… 749
15.7 铁磁性金属的磁化和退磁 …… 751
15.8 软磁材料 …… 752
15.8.1 软磁材料的理想性能 …… 753
15.8.2 软磁材料的能量损失 …… 753
15.8.3 铁-硅合金 …… 754
15.8.4 金属玻璃 …… 755
15.8.5 镍-铁合金 …… 756

15.9 硬磁材料 …… 759
15.9.1 硬磁材料的性能 …… 759
15.9.2 铝镍钴（Alnico）合金 …… 761
15.9.3 稀土合金 …… 763
15.9.4 钕-铁-硼磁合金 …… 765
15.9.5 铁-铬-钴磁合金 …… 765
15.10 铁氧体 …… 767
15.10.1 软磁铁氧体 …… 767
15.10.2 硬磁铁氧体 …… 771
15.11 第15章小结 …… 771
15.12 定义 …… 772
15.13 习题 …… 775
附录Ⅰ：部分元素的一些性质 …… 780
附录Ⅱ：元素的离子半径 …… 782
习题解答 …… 784

TABLE OF CONTENTS

Preface

CHAPTER **1**
Introduction to Materials Science and Engineering 2

- **1.1** Materials and Engineering 3
- **1.2** Materials Science and Engineering 6
- **1.3** Types of Materials 8
  - **1.3.1** *Metallic Materials 8*
  - **1.3.2** *Polymeric Materials 10*
  - **1.3.3** *Ceramic Materials 11*
  - **1.3.4** *Composite Materials 13*
  - **1.3.5** *Electronic Materials 14*
- **1.4** Competition Among Materials 15
- **1.5** Recent Advances in Materials Science and Technology and Future Trends 17
  - **1.5.1** *Smart Materials 17*
  - **1.5.2** *Nanomaterials 19*
- **1.6** Design and Selection 19
- **1.7** Summary 20
- **1.8** Definitions 21
- **1.9** Problems 22

CHAPTER **2**
Atomic Structure and Bonding 24

- **2.1** Atomic Structure and Subatomic Particles 25
- **2.2** Atomic Numbers, Mass Numbers, and Atomic Masses 28
- **2.3** The Electronic Structure of Atoms 31
  - **2.3.1** *Planck's Quantum Theory and Electromagnetic Radiation 31*
  - **2.3.2** *Bohr's Theory of the Hydrogen Atom 34*
  - **2.3.3** *The Uncertainty Principle and Schrodinger's Wave Functions 37*
  - **2.3.4** *Quantum Numbers, Energy Levels, and Atomic Orbitals 40*
  - **2.3.5** *The Energy State of Multielectron Atoms 43*
  - **2.3.6** *The Quantum-Mechanical Model and the Periodic Table 44*
- **2.4** Periodic Variations in Atomic Size, Ionization Energy, and Electron Affinity 49
  - **2.4.1** *Trends in Atomic Size 49*
  - **2.4.2** *Trends in Ionization Energy 49*
  - **2.4.3** *Trends in Electron Affinity 52*
  - **2.4.4** *Metals, Metalloids, and Nonmetals 52*
- **2.5** Primary Bonds 54
  - **2.5.1** *Ionic Bonds 55*
  - **2.5.2** *Covalent Bonds 61*
  - **2.5.3** *Metallic Bonds 68*
  - **2.5.4** *Mixed Bonding 70*
- **2.6** Secondary Bonds 71
- **2.7** Summary 74
- **2.8** Definitions 75
- **2.9** Problems 77

CHAPTER **3**
Crystal and Amorphous Structure in Materials 84

- **3.1** The Space Lattice and Unit Cells 85
- **3.2** Crystal Systems and Bravais Lattices 86
- **3.3** Principal Metallic Crystal Structures 87
  - **3.3.1** *Body-Centered Cubic (BCC) Crystal Structure 89*
  - **3.3.2** *Face-Centered Cubic (FCC) Crystal Structure 92*
  - **3.3.3** *Hexagonal Close-Packed (HCP) Crystal Structure 93*
- **3.4** Atom Positions in Cubic Unit Cells 95
- **3.5** Directions in Cubic Unit Cells 96

3.6 Miller Indices for Crystallographic Planes in Cubic Unit Cells 100

3.7 Crystallographic Planes and Directions in Hexagonal Crystal Structure 105

3.7.1 *Indices for Crystal Planes in HCP Unit Cells 105*

3.7.2 *Direction Indices in HCP Unit Cells 106*

3.8 Comparison of FCC, HCP, and BCC Crystal Structures 108

3.8.1 *FCC and HCP Crystal Structures 108*

3.8.2 *BCC Crystal Structure 110*

3.9 Volume, Planar, and Linear Density Unit-Cell Calculations 110

3.9.1 *Volume Density 110*

3.9.2 *Planar Atomic Density 111*

3.9.3 *Linear Atomic Density 113*

3.10 Polymorphism or Allotropy 114

3.11 Crystal Structure Analysis 115

3.11.1 *X-Ray Sources 116*

3.11.2 *X-Ray Diffraction 117*

3.11.3 *X-Ray Diffraction Analysis of Crystal Structures 119*

3.12 Amorphous Materials 125

3.13 Summary 126

3.14 Definitions 127

3.15 Problems 128

CHAPTER **4**

Solidification and Crystalline Imperfections 136

4.1 Solidification of Metals 137

4.1.1 *The Formation of Stable Nuclei in Liquid Metals 139*

4.1.2 *Growth of Crystals in Liquid Metal and Formation of a Grain Structure 144*

4.1.3 *Grain Structure of Industrial Castings 145*

4.2 Solidification of Single Crystals 146

4.3 Metallic Solid Solutions 150

4.3.1 *Substitutional Solid Solutions 151*

4.3.2 *Interstitial Solid Solutions 153*

4.4 Crystalline Imperfections 155

4.4.1 *Point Defects 155*

4.4.2 *Line Defects (Dislocations) 156*

4.4.3 *Planar Defects 159*

4.4.4 *Volume Defects 162*

4.5 Experimental Techniques for Identification of Microstructure and Defects 163

4.5.1 *Optical Metallography, ASTM Grain Size, and Grain Diameter Determination 163*

4.5.2 *Scanning Electron Microscopy (SEM) 168*

4.5.3 *Transmission Electron Microscopy (TEM) 169*

4.5.4 *High-Resolution Transmission Electron Microscopy (HRTEM) 170*

4.5.5 *Scanning Probe Microscopes and Atomic Resolution 173*

4.6 Summary 176

4.7 Definitions 177

4.8 Problems 178

CHAPTER **5**

Thermally Activated Processes and Diffusion in Solids 186

5.1 Rate Processes in Solids 187

5.2 Atomic Diffusion in Solids 191

5.2.1 *Diffusion in Solids in General 191*

5.2.2 *Diffusion Mechanisms 191*

5.2.3 *Steady-State Diffusion 193*

5.2.4 *Non–Steady-State Diffusion 196*

5.3 Industrial Applications of Diffusion Processes 198

5.3.1 *Case Hardening of Steel by Gas Carburizing 198*

5.3.2 *Impurity Diffusion into Silicon Wafers for Integrated Circuits 202*

5.4 Effect of Temperature on Diffusion in Solids 204

5.5 Summary 208

5.6 Definitions 208

5.7 Problems 209

CHAPTER 6

Mechanical Properties of Metals I 214

6.1 The Processing of Metals and Alloys 215
  6.1.1 *The Casting of Metals and Alloys 215*
  6.1.2 *Hot and Cold Rolling of Metals and Alloys 217*
  6.1.3 *Extrusion of Metals and Alloys 221*
  6.1.4 *Forging 222*
  6.1.5 *Other Metal-Forming Processes 224*
6.2 Stress and Strain in Metals 225
  6.2.1 *Elastic and Plastic Deformation 225*
  6.2.2 *Engineering Stress and Engineering Strain 226*
  6.2.3 *Poisson's Ratio 228*
  6.2.4 *Shear Stress and Shear Strain 228*
6.3 The Tensile Test and the Engineering Stress-Strain Diagram 230
  6.3.1 *Mechanical Property Data Obtained from the Tensile Test and the Engineering Stress-Strain Diagram 232*
  6.3.2 *Comparison of Engineering Stress-Strain Curves for Selected Alloys 237*
  6.3.3 *True Stress and True Strain 237*
6.4 Hardness and Hardness Testing 239
6.5 Plastic Deformation of Metal Single Crystals 240
  6.5.1 *Slipbands and Slip Lines on the Surface of Metal Crystals 240*
  6.5.2 *Plastic Deformation in Metal Crystals by the Slip Mechanism 242*
  6.5.3 *Slip Systems 244*
  6.5.4 *Critical Resolved Shear Stress for Metal Single Crystals 249*
  6.5.5 *Schmid's Law 250*
  6.5.6 *Twinning 252*
6.6 Plastic Deformation of Polycrystalline Metals 254
  6.6.1 *Effect of Grain Boundaries on the Strength of Metals 254*
  6.6.2 *Effect of Plastic Deformation on Grain Shape and Dislocation Arrangements 256*
  6.6.3 *Effect of Cold Plastic Deformation on Increasing the Strength of Metals 258*
6.7 Solid-Solution Strengthening of Metals 259
6.8 Recovery and Recrystallization of Plastically Deformed Metals 261
  6.8.1 *Structure of a Heavily Cold-Worked Metal before Reheating 262*
  6.8.2 *Recovery 263*
  6.8.3 *Recrystallization 264*
6.9 Superplasticity in Metals 268
6.10 Nanocrystalline Metals 270
6.11 Summary 271
6.12 Definitions 272
6.13 Problems 273

CHAPTER 7

Mechanical Properties of Metals II 280

7.1 Fracture of Metals 281
  7.1.1 *Ductile Fracture 282*
  7.1.2 *Brittle Fracture 283*
  7.1.3 *Toughness and Impact Testing 286*
  7.1.4 *Ductile to Brittle Transition Temperature 286*
  7.1.5 *Fracture Toughness 289*
7.2 Fatigue of Metals 291
  7.2.1 *Cyclic Stresses 295*
  7.2.2 *Basic Structural Changes that Occur in a Ductile Metal in the Fatigue Process 296*
  7.2.3 *Some Major Factors that Affect the Fatigue Strength of a Metal 297*
7.3 Fatigue Crack Propagation Rate 298
  7.3.1 *Correlation of Fatigue Crack Propagation with Stress and Crack Length 298*
  7.3.2 *Fatigue Crack Growth Rate versus Stress-Intensity Factor Range Plots 300*
  7.3.3 *Fatigue Life Calculations 302*
7.4 Creep and Stress Rupture of Metals 304
  7.4.1 *Creep of Metals 304*

- **7.4.2** *The Creep Test 306*
- **7.4.3** *Creep-Rupture Test 307*

7.5 Summary 308
7.6 Definitions 309
7.7 Problems 309

CHAPTER 8
Phase Diagrams 316

8.1 Phase Diagrams of Pure Substances 317
8.2 Gibbs Phase Rule 319
8.3 Cooling Curves 320
8.4 Binary Isomorphous Alloy Systems 321
8.5 The Lever Rule 324
8.6 Nonequilibrium Solidification of Alloys 328
8.7 Binary Eutectic Alloy Systems 331
8.8 Binary Peritectic Alloy Systems 339
8.9 Binary Monotectic Systems 344
8.10 Invariant Reactions 345
8.11 Phase Diagrams with Intermediate Phases and Compounds 347
8.12 Ternary Phase Diagrams 351
8.13 Summary 354
8.14 Definitions 355
8.15 Problems 357

CHAPTER 9
Engineering Alloys 366

9.1 Production of Iron and Steel 368
- **9.1.1** *Production of Pig Iron in a Blast Furnace 368*
- **9.1.2** *Steelmaking and Processing of Major Steel Product Forms 369*

9.2 The Iron-Carbon System 371
- **9.2.1** *The Iron–Iron-Carbide Phase Diagram 371*
- **9.2.2** *Solid Phases in the Fe-Fe$_3$C Phase Diagram 371*
- **9.2.3** *Invariant Reactions in the Fe-Fe$_3$C Phase Diagram 372*
- **9.2.4** *Slow Cooling of Plain-Carbon Steels 374*

9.3 Heat Treatment of Plain-Carbon Steels 381
- **9.3.1** *Martensite 381*
- **9.3.2** *Isothermal Decomposition of Austenite 386*
- **9.3.3** *Continuous-Cooling Transformation Diagram for a Eutectoid Plain-Carbon Steel 391*
- **9.3.4** *Annealing and Normalizing of Plain-Carbon Steels 394*
- **9.3.5** *Tempering of Plain-Carbon Steels 395*
- **9.3.6** *Classification of Plain-Carbon Steels and Typical Mechanical Properties 399*

9.4 Low-Alloy Steels 400
- **9.4.1** *Classification of Alloy Steels 400*
- **9.4.2** *Distribution of Alloying Elements in Alloy Steels 402*
- **9.4.3** *Effects of Alloying Elements on the Eutectoid Temperature of Steels 403*
- **9.4.4** *Hardenability 404*
- **9.4.5** *Typical Mechanical Properties and Applications for Low-Alloy Steels 409*

9.5 Aluminum Alloys 409
- **9.5.1** *Precipitation Strengthening (Hardening) 411*
- **9.5.2** *General Properties of Aluminum and Its Production 418*
- **9.5.3** *Wrought Aluminum Alloys 419*
- **9.5.4** *Aluminum Casting Alloys 424*

9.6 Summary 426
9.7 Definitions 427
9.8 Problems 428

CHAPTER 10
Polymeric Materials 436

10.1 Introduction 437

  - **10.1.1** *Thermoplastics 438*
  - **10.1.2** *Thermosetting Plastics (Thermosets) 438*
- **10.2** Polymerization Reactions 439
  - **10.2.1** *Covalent Bonding Structure of an Ethylene Molecule 439*
  - **10.2.2** *Covalent Bonding Structure of an Activated Ethylene Molecule 440*
  - **10.2.3** *General Reaction for the Polymerization of Polyethylene and the Degree of Polymerization 441*
  - **10.2.4** *Chain Polymerization Steps 441*
  - **10.2.5** *Average Molecular Weight for Thermoplastics 443*
  - **10.2.6** *Functionality of a Monomer 444*
  - **10.2.7** *Structure of Noncrystalline Linear Polymers 444*
  - **10.2.8** *Vinyl and Vinylidene Polymers 446*
  - **10.2.9** *Homopolymers and Copolymers 447*
  - **10.2.10** *Other Methods of Polymerization 450*
- **10.3** Industrial Polymerization Methods 452
- **10.4** Crystallinity and Stereoisomerism in Some Thermoplastics 454
  - **10.4.1** *Solidification of Noncrystalline Thermoplastics 454*
  - **10.4.2** *Solidification of Partly Crystalline Thermoplastics 454*
  - **10.4.3** *Structure of Partly Crystalline Thermoplastic Materials 456*
  - **10.4.4** *Stereoisomerism in Thermoplastics 457*
  - **10.4.5** *Ziegler and Natta Catalysts 458*
- **10.5** Processing of Plastic Materials 459
  - **10.5.1** *Processes Used for Thermoplastic Materials 460*
  - **10.5.2** *Processes Used for Thermosetting Materials 464*
- **10.6** General-Purpose Thermoplastics 466
  - **10.6.1** *Polyethylene 468*
  - **10.6.2** *Polyvinyl Chloride and Copolymers 471*
  - **10.6.3** *Polypropylene 473*
  - **10.6.4** *Polystyrene 473*
  - **10.6.5** *Polyacrylonitrile 474*
  - **10.6.6** *Styrene-Acrylonitrile (SAN) 475*
  - **10.6.7** *ABS 475*
  - **10.6.8** *Polymethyl Methacrylate (PMMA) 477*
  - **10.6.9** *Fluoroplastics 478*
- **10.7** Engineering Thermoplastics 479
  - **10.7.1** *Polyamides (Nylons) 480*
  - **10.7.2** *Polycarbonate 483*
  - **10.7.3** *Phenylene Oxide–Based Resins 484*
  - **10.7.4** *Acetals 485*
  - **10.7.5** *Thermoplastic Polyesters 486*
  - **10.7.6** *Polyphenylene Sulfide 487*
  - **10.7.7** *Polyetherimide 488*
  - **10.7.8** *Polymer Alloys 488*
- **10.8** Thermosetting Plastics (Thermosets) 489
  - **10.8.1** *Phenolics 491*
  - **10.8.2** *Epoxy Resins 492*
  - **10.8.3** *Unsaturated Polyesters 494*
  - **10.8.4** *Amino Resins (Ureas and Melamines) 495*
- **10.9** Summary 497
- **10.10** Definitions 498
- **10.11** Problems 500

CHAPTER **11**

Ceramics 510

- **11.1** Introduction 511
- **11.2** Simple Ceramic Crystal Structures 513
  - **11.2.1** *Ionic and Covalent Bonding in Simple Ceramic Compounds 513*
  - **11.2.2** *Simple Ionic Arrangements Found in Ionically Bonded Solids 514*
  - **11.2.3** *Cesium Chloride (CsCl) Crystal Structure 517*
  - **11.2.4** *Sodium Chloride (NaCl) Crystal Structure 518*
  - **11.2.5** *Interstitial Sites in FCC and HCP Crystal Lattices 522*
  - **11.2.6** *Zinc Blende (ZnS) Crystal Structure 524*
  - **11.2.7** *Calcium Fluoride (CaF_2) Crystal Structure 526*
  - **11.2.8** *Antifluorite Crystal Structure 528*
  - **11.2.9** *Corundum (Al_2O_3) Crystal Structure 528*

- **11.2.10** *Spinel ($MgAl_2O_4$) Crystal Structure 528*
- **11.2.11** *Perovskite ($CaTiO_3$) Crystal Structure 528*
- **11.2.12** *Carbon and Its Allotropes 529*

11.3 Silicate Structures 533
- **11.3.1** *Basic Structural Unit of the Silicate Structures 533*
- **11.3.2** *Island, Chain, and Ring Structures of Silicates 533*
- **11.3.3** *Sheet Structures of Silicates 533*
- **11.3.4** *Silicate Networks 535*

11.4 Processing of Ceramics 536
- **11.4.1** *Materials Preparation 537*
- **11.4.2** *Forming 537*
- **11.4.3** *Thermal Treatments 542*

11.5 Traditional and Engineering Ceramics 544
- **11.5.1** *Traditional Ceramics 544*
- **11.5.2** *Engineering Ceramics 547*

11.6 Mechanical Properties of Ceramics 549
- **11.6.1** *General 549*
- **11.6.2** *Mechanisms for the Deformation of Ceramic Materials 549*
- **11.6.3** *Factors Affecting the Strength of Ceramic Materials 550*
- **11.6.4** *Toughness of Ceramic Materials 551*
- **11.6.5** *Transformation Toughening of Partially Stabilized Zirconia (PSZ) 553*
- **11.6.6** *Fatigue Failure of Ceramics 553*
- **11.6.7** *Ceramic Abrasive Materials 555*

11.7 Thermal Properties of Ceramics 556
- **11.7.1** *Ceramic Refractory Materials 557*
- **11.7.2** *Acidic Refractories 558*
- **11.7.3** *Basic Refractories 558*
- **11.7.4** *Ceramic Tile Insulation for the Space Shuttle Orbiter 558*

11.8 Glasses 558
- **11.8.1** *Definition of a Glass 560*
- **11.8.2** *Glass Transition Temperature 560*
- **11.8.3** *Structure of Glasses 561*
- **11.8.4** *Compositions of Glasses 562*
- **11.8.5** *Viscous Deformation of Glasses 564*
- **11.8.6** *Forming Methods for Glasses 566*
- **11.8.7** *Tempered Glass 568*
- **11.8.8** *Chemically Strengthened Glass 568*

11.9 Ceramic Coatings and Surface Engineering 570
- **11.9.1** *Silicate Glasses 570*
- **11.9.2** *Oxides and Carbides 570*

11.10 Nanotechnology and Ceramics 571

11.11 Summary 573

11.12 Definitions 574

11.13 Problems 575

CHAPTER **12**

Composite Materials 582

12.1 Introduction 583

12.2 Fibers for Reinforced-Plastic Composite Materials 584
- **12.2.1** *Glass Fibers for Reinforcing Plastic Resins 584*
- **12.2.2** *Carbon Fibers for Reinforced Plastics 587*
- **12.2.3** *Aramid Fibers for Reinforcing Plastic Resins 589*
- **12.2.4** *Comparison of Mechanical Properties of Carbon, Aramid, and Glass Fibers for Reinforced-Plastic Composite Materials 589*

12.3 Fiber-Reinforced–Plastic Composite Materials 591
- **12.3.1** *Matrix Materials for Fiber-Reinforced–Plastic Composite Materials 591*
- **12.3.2** *Fiber-Reinforced–Plastic Composite Materials 592*
- **12.3.3** *Equations for Elastic Modulus of a Lamellar Continuous-Fiber–Plastic Matrix Composite for Isostrain and Isostress Conditions 596*

12.4 Open-Mold Processes for Fiber-Reinforced–Plastic Composite Materials 601
  - **12.4.1** *Hand Lay-Up Process 601*
  - **12.4.2** *Spray-Up Process 601*
  - **12.4.3** *Vacuum Bag–Autoclave Process 602*
  - **12.4.4** *Filament-Winding Process 603*

12.5 Closed-Mold Processes for Fiber-Reinforced–Plastic Composite Materials 604
  - **12.5.1** *Compression and Injection Molding 604*
  - **12.5.2** *The Sheet-Molding Compound (SMC) Process 605*
  - **12.5.3** *Continuous-Pultrusion Process 606*

12.6 Metal-Matrix and Ceramic-Matrix Composites 606
  - **12.6.1** *Metal-Matrix Composites (MMCs) 606*
  - **12.6.2** *Ceramic-Matrix Composites (CMCs) 608*
  - **12.6.3** *Ceramic Composites and Nanotechnology 613*

12.7 Summary 613

12.8 Definitions 614

12.9 Problems 616

CHAPTER **13**
Electrical Properties of Materials 624

13.1 Electrical Conduction in Metals 625
  - **13.1.1** *The Classic Model for Electrical Conduction in Metals 625*
  - **13.1.2** *Ohm's Law 627*
  - **13.1.3** *Drift Velocity of Electrons in a Conducting Metal 631*
  - **13.1.4** *Electrical Resistivity of Metals 632*

13.2 Energy-Band Model For Electrical Conduction 636
  - **13.2.1** *Energy-Band Model for Metals 636*
  - **13.2.2** *Energy-Band Model for Insulators 638*

13.3 Intrinsic Semiconductors 638
  - **13.3.1** *The Mechanism of Electrical Conduction in Intrinsic Semiconductors 638*
  - **13.3.2** *Electrical Charge Transport in the Crystal Lattice of Pure Silicon 639*
  - **13.3.3** *Energy-Band Diagram for Intrinsic Elemental Semiconductors 640*
  - **13.3.4** *Quantitative Relationships for Electrical Conduction in Elemental Intrinsic Semiconductors 641*
  - **13.3.5** *Effect of Temperature on Intrinsic Semiconductivity 643*

13.4 Extrinsic Semiconductors 645
  - **13.4.1** *n-Type (Negative-Type) Extrinsic Semiconductors 645*
  - **13.4.2** *p-Type (Positive-Type) Extrinsic Semiconductors 647*
  - **13.4.3** *Doping of Extrinsic Silicon Semiconductor Material 649*
  - **13.4.4** *Effect of Doping on Carrier Concentrations in Extrinsic Semiconductors 649*
  - **13.4.5** *Effect of Total Ionized Impurity Concentration on the Mobility of Charge Carriers in Silicon at Room Temperature 652*
  - **13.4.6** *Effect of Temperature on the Electrical Conductivity of Extrinsic Semiconductors 653*

13.5 Semiconductor Devices 655
  - **13.5.1** *The pn Junction 656*
  - **13.5.2** *Some Applications for pn Junction Diodes 659*
  - **13.5.3** *The Bipolar Junction Transistor 660*

13.6 Microelectronics 662
  - **13.6.1** *Microelectronic Planar Bipolar Transistors 662*
  - **13.6.2** *Microelectronic Planar Field-Effect Transistors 663*

- 13.6.3 *Fabrication of Microelectronic Integratea Circuits 666*

13.7 Compound Semiconductors 673

13.8 Electrical Properties of Ceramics 676
- 13.8.1 *Basic Properties of Dielectrics 676*
- 13.8.2 *Ceramic Insulator Materials 678*
- 13.8.3 *Ceramic Materials for Capacitors 679*
- 13.8.4 *Ceramic Semiconductors 680*
- 13.8.5 *Ferroelectric Ceramics 682*

13.9 Nanoelectronics 685

13.10 Summary 686

13.11 Definitions 687

13.12 Problems 690

CHAPTER 14
Optical Properties and Superconductive Material 696

14.1 Introduction 697

14.2 Light and the Electromagnetic Spectrum 697

14.3 Refraction of Light 699
- 14.3.1 *Index of Refraction 699*
- 14.3.2 *Snell's Law of Light Refraction 701*

14.4 Absorption, Transmission, and Reflection of Light 702
- 14.4.1 *Metals 702*
- 14.4.2 *Silicate Glasses 703*
- 14.4.3 *Plastics 704*
- 14.4.4 *Semiconductors 706*

14.5 Luminescence 707
- 14.5.1 *Photoluminescence 708*
- 14.5.2 *Cathodoluminescence 708*

14.6 Stimulated Emission of Radiation and Lasers 710
- 14.6.1 *Types of Lasers 712*

14.7 Optical Fibers 714
- 14.7.1 *Light Loss in Optical Fibers 714*
- 14.7.2 *Single-Mode and Multimode Optical Fibers 715*
- 14.7.3 *Fabrication of Optical Fibers 716*
- 14.7.4 *Modern Optical-Fiber Communication Systems 718*

14.8 Superconducting Materials 719
- 14.8.1 *The Superconducting State 719*
- 14.8.2 *Magnetic Properties of Superconductors 720*
- 14.8.3 *Current Flow and Magnetic Fields in Superconductors 722*
- 14.8.4 *High-Current, High-Field Superconductors 723*
- 14.8.5 *High Critical Temperature (T_c) Superconducting Oxides 725*

14.9 Definitions 727

14.10 Problems 728

CHAPTER 15
Magnetic Properties 732

15.1 Introduction 733

15.2 Magnetic Fields and Quantities 733
- 15.2.1 *Magnetic Fields 733*
- 15.2.2 *Magnetic Induction 736*
- 15.2.3 *Magnetic Permeability 736*
- 15.2.4 *Magnetic Susceptibility 738*

15.3 Types of Magnetism 738
- 15.3.1 *Diamagnetism 739*
- 15.3.2 *Paramagnetism 739*
- 15.3.3 *Ferromagnetism 739*
- 15.3.4 *Magnetic Moment of a Single Unpaired Atomic Electron 741*
- 15.3.5 *Antiferromagnetism 743*
- 15.3.6 *Ferrimagnetism 743*

15.4 Effect of Temperature on Ferromagnetism 743

15.5 Ferromagnetic Domains 744

15.6 Types of Energies that Determine the Structure of Ferromagnetic Domains 746
- 15.6.1 *Exchange Energy 746*
- 15.6.2 *Magnetostatic Energy 747*
- 15.6.3 *Magnetocrystalline Anisotropy Energy 747*
- 15.6.4 *Domain Wall Energy 748*

15.6.5 *Magnetostrictive Energy 749*

15.7 The Magnetization and Demagnetization of a Ferromagnetic Metal 751

15.8 Soft Magnetic Materials 752

15.8.1 *Desirable Properties for Soft Magnetic Materials 753*

15.8.2 *Energy Losses for Soft Magnetic Materials 753*

15.8.3 *Iron-Silicon Alloys 754*

15.8.4 *Metallic Glasses 755*

15.8.5 *Nickel-Iron Alloys 756*

15.9 Hard Magnetic Materials 759

15.9.1 *Properties of Hard Magnetic Materials 759*

15.9.2 *Alnico Alloys 761*

15.9.3 *Rare Earth Alloys 763*

15.9.4 *Neodymium-Iron-Boron Magnetic Alloys 765*

15.9.5 *Iron-Chromium-Cobalt Magnetic Alloys 765*

15.10 Ferrites 767

15.10.1 *Magnetically Soft Ferrites 767*

15.10.2 *Magnetically Hard Ferrites 771*

15.11 Summary 771

15.12 Definitions 772

15.13 Problems 775

APPENDIX **I**
Some Properties of Selected Elements 780

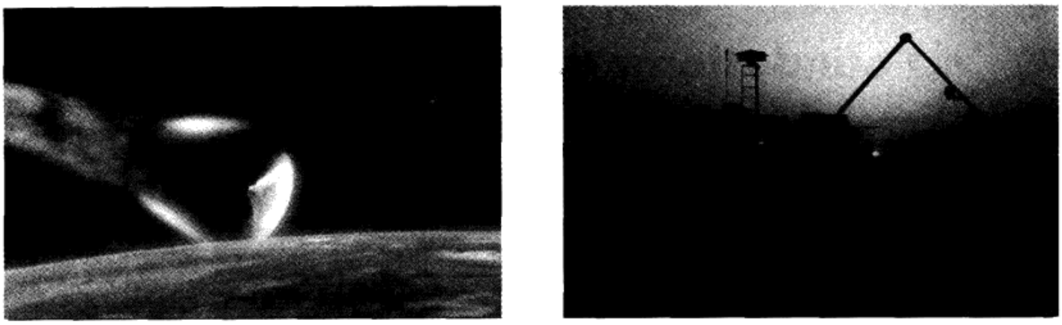
APPENDIX **II**
Ionic Radii of the Elements 782

Answers 784

Foundations of Materials Science and Engineering

CHAPTER 1

Introduction to Materials Science and Engineering



(*Courtesy of NASA.*)

The Phoenix Mars Lander is the "robot scientist" behind the most recent scientific quest by NASA's Mars Exploration Program. Two major scientific goals of the Phoenix mission are to establish if life ever arose on Mars and understand Mars' climate behavior. The spacecraft is a masterpiece of engineering representing our human desire to gain knowledge. Imagine the materials science and engineering challenges in designing the craft to withstand, survive, and function effectively under a variety of extreme conditions. For instance, during the launch, the spacecraft and its sensitive instruments experience tremendous loads: during the cruise stage, the spacecraft must withstand solar storms and micrometeorite impact; during entry, descent, and landing, the temperature will rise by several thousands of degrees, and it will be yanked by a tremendous deceleration force when the parachute is deployed; and finally during operation, it must endure the extreme cold temperatures of the Martian arctic and the Martian dust storms.

The Lander is equipped with a suite of engineering tools and scientific instruments. The major instruments aboard the Lander include (1) a camera-enabled robotic arm (built by Jet Propulsion Laboratory [JPL], University of Arizona, and Max Planck Institute in Germany), (2) microscopy, electrochemistry, and conductivity analyzer instruments (JPL), (3) thermal and evolved gas analyzer (University of Arizona and University of Texas Dallas), (4) various imaging systems, and (5) a meteorological station (Canadian Space Agency). All major categories of materials including metals, polymer, ceramic, composite, and electronic materials are utilized in the structure of the Lander and its instruments.

The Phoenix Mars Lander mission uses our most sophisticated technologies, knowledge, and skills in the field of materials science and engineering to generate new knowledge about Mars that may pave the way for human exploration of space and habitation of other planets. ■

LEARNING OBJECTIVES

By the end of this chapter, students will be able to . . .

1. Describe the subject of materials science and engineering as a scientific discipline.
2. Cite the primary classification of solid materials.
3. Give distinctive features of each group of materials.
4. Cite one material from each group. Give some applications of different types of materials.
5. Evaluate how much you know and how much you do not know about materials.
6. Establish the importance of materials science and engineering in selection of materials for various applications.

1.1 MATERIALS AND ENGINEERING

Humankind, **materials,** and engineering have evolved over the passage of time and are continuing to do so. All of us live in a world of dynamic change, and materials are no exception. The advancement of civilization has historically depended on the improvement of materials to work with. Prehistoric humans were restricted to naturally accessible materials such as stone, wood, bones, and fur. Over time, they moved from the materials Stone Age into the newer Copper (Bronze) and Iron Ages. Note that this advance did not take place uniformly everywhere—we shall see that this is true in nature even down to the microscopic scale. Even today we are restricted to the materials we can obtain from Earth's crust and atmosphere (Table 1.1). According to Webster's dictionary, materials may be defined as substances of which something is composed or made. Although this definition is broad, from an engineering application point of view, it covers almost all relevant situations.

Table 1.1 The most common elements in planet Earth's crust and atmosphere by weight percentage and volume

Element	Weight percentage of the Earth's crust
Oxygen (O)	46.60
Silicon (Si)	27.72
Aluminum (Al)	8.13
Iron (Fe)	5.00
Calcium (Ca)	3.63
Sodium (Na)	2.83
Potassium (K)	2.70
Magnesium (Mg)	2.09
Total	98.70
Gas	**Percent of dry air by volume**
Nitrogen (N_2)	78.08
Oxygen (O_2)	20.95
Argon (Ar)	0.93
Carbon dioxide (CO_2)	0.03

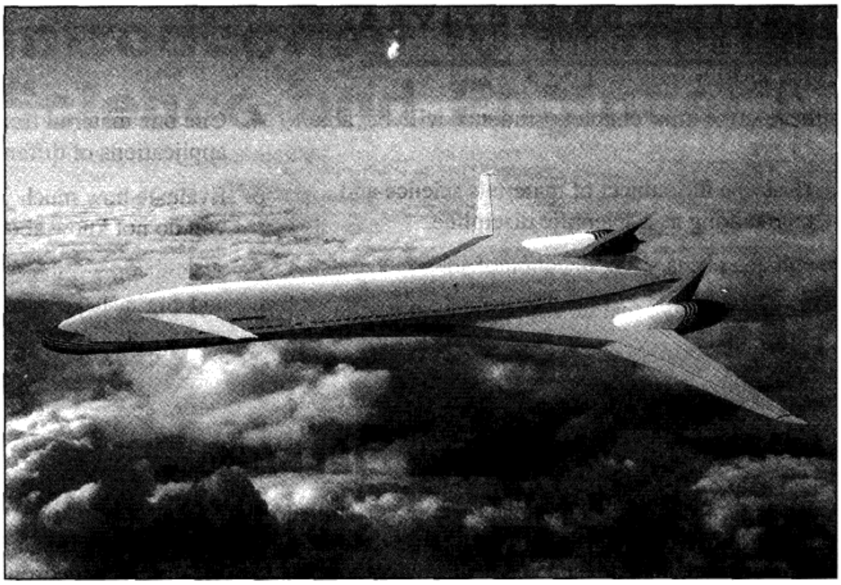


Figure 1.1
High-speed civil transport image shows the Hyper-X at Mach 7 with the engines operating. Rings indicate surface flow speeds.
(© *The Boeing Company.*)

The production and processing of materials into finished goods constitutes a large part of our present economy. Engineers design most manufactured products and the processing systems required for their production. Since products require materials, engineers should be knowledgeable about the internal structure and properties of materials so that they can choose the most suitable ones for each application and develop the best processing methods.

Research and development engineers create new materials or modify the properties of existing ones. Design engineers use existing, modified, or new materials to design and create new products and systems. Sometimes design engineers have a problem in their design that requires a new material to be created by research scientists and engineers. For example, engineers designing a *high-speed civil transport* (HSCT) (Fig. 1.1) will have to develop new high-temperature materials that will withstand temperatures as high as 1800°C (3272°F) so that airspeeds as high as Mach 12 to 25 can be attained.[1] Research is currently underway to develop new ceramic-matrix composites, refractory intermetallic compounds, and single-crystal superalloys for this and other similar applications.

One area that demands the most from materials scientists and engineers is space exploration. The design and construction of the *International Space Station*

---

[1] Mach 1 equals the speed of sound in air.

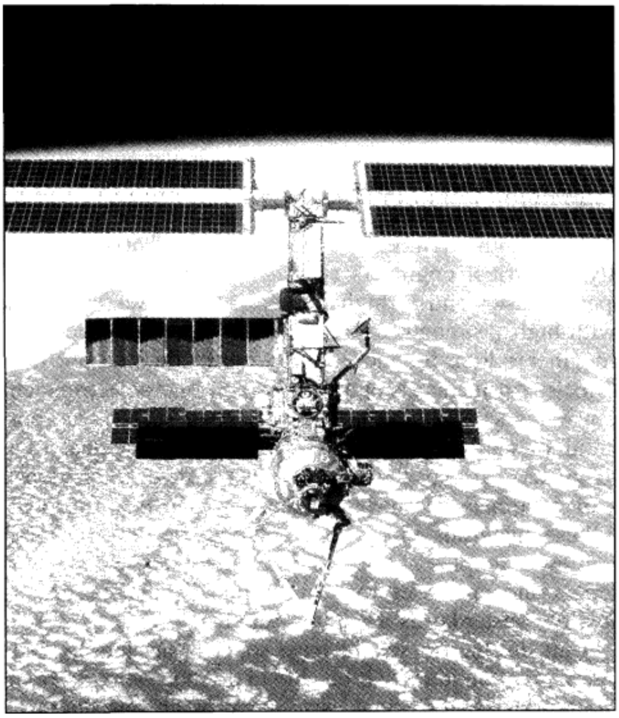


Figure 1.2
The International Space Station.
(© *Stocktrek/age fotostock.*)

(ISS) and *Mars Exploration Rover* (MER) missions are examples of space research and exploration activities that require the absolute best from our materials scientists and engineers. The construction of ISS, a large research laboratory moving at a speed of 27,000 km/h through space, required selection of materials that would function in an environment far different than ours on earth (Fig. 1.2). The materials must be lightweight to minimize payload weight during liftoff. The outer shell must protect against the impact of tiny meteoroids and man-made debris. The internal air pressure of roughly 15 psi is constantly stressing the modules. Additionally, the modules must withstand the massive stresses at launch. Materials selection for MERs is also a challenge, especially considering that they must survive an environment in which night temperatures could be as low as −96°C. These and other constraints push the limits of material selection in the design of complex systems.

We must remember that materials usage and engineering designs are constantly changing. This change continues to accelerate. No one can predict the long-term future advances in material design and usage. In 1943 the prediction was made that successful people in the United States would own their own autogyros (auto-airplanes).

How wrong that prediction was! At the same time, the transistor, the integrated circuit, and television (color and high definition included) were neglected. Thirty years ago, many people would not have believed that some day computers would become a common household item similar to a telephone or a refrigerator. And today, we still find it hard to believe that some day space travel will be commercialized and we may even colonize Mars. Nevertheless, science and engineering push and transform our most unachievable dreams to reality.

The search for new materials goes on continuously. For example, mechanical engineers search for higher-temperature materials so that jet engines can operate more efficiently. Electrical engineers search for new materials so that electronic devices can operate faster and at higher temperatures. Aerospace engineers search for materials with higher strength-to-weight ratios for aerospace vehicles. Chemical and materials engineers look for more highly corrosion-resistant materials. Various industries look for smart materials and devices and microelectromechanical systems (MEMs) to be used as sensors and actuators in their respective applications. More recently, the field of nanomaterials has attracted a great deal of attention from scientists and engineers all over the world. Novel structural, chemical, and mechanical properties of nanomaterials have opened new and exciting possibilities in the application of these materials to a variety of engineering and medical problems. These are only a few examples of the search by engineers and scientists for new and improved materials and processes for a multitude of applications. In many cases, what was impossible yesterday is a reality today!

Engineers in all disciplines should have some basic and applied knowledge of engineering materials so that they will be able to do their work more effectively when using them. The purpose of this book is to serve as an introduction to the internal structure, properties, processing, and applications of engineering materials. Because of the enormous amount of information available about engineering materials and due to the limitations of this book, the presentation has had to be selective.

1.2 MATERIALS SCIENCE AND ENGINEERING

Materials science is primarily concerned with the search for basic knowledge about the internal structure, properties, and processing of materials. **Materials engineering** is mainly concerned with the use of fundamental and applied knowledge of materials so that the materials can be converted into products needed or desired by society. The term *materials science and engineering* combines both materials science and materials engineering and is the subject of this book. Materials science is at the basic knowledge end of the materials knowledge spectrum and materials engineering is at the applied knowledge end, and there is no demarcation line between the two (Fig. 1.3).

Figure 1.4 shows a three-ringed diagram that indicates the relationship among the basic sciences (and mathematics), materials science and engineering, and the other engineering disciplines. The basic sciences are located within the inner ring or core of the diagram, while the various engineering disciplines (mechanical, electri-

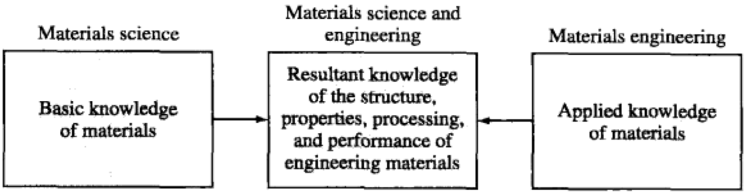

Materials science
Materials science and engineering
Materials engineering
Basic knowledge of materials
Resultant knowledge of the structure, properties, processing, and performance of engineering materials
Applied knowledge of materials

Figure 1.3
Materials knowledge spectrum. Using the combined knowledge of materials from materials science and materials engineering enables engineers to convert materials into the products needed by society.

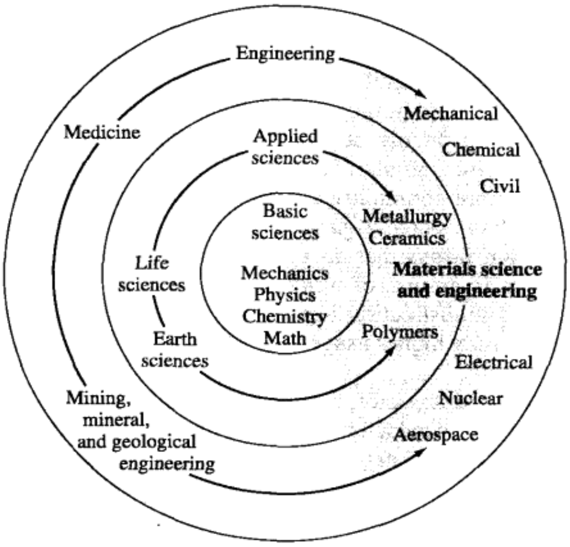

Engineering
Mechanical
Chemical
Civil
Medicine
Applied sciences
Basic sciences
Metallurgy
Ceramics
Life sciences
Mechanics
Physics
Chemistry
Math
Materials science and engineering
Earth sciences
Polymers
Electrical
Nuclear
Mining, mineral, and geological engineering
Aerospace

Figure 1.4
This diagram illustrates how materials science and engineering form a bridge of knowledge from the basic sciences to the engineering disciplines.
(Reprinted with permission from National Academy of Sciences, courtesy of National Academic Press.)

cal, civil, chemical, etc.) are located in the outermost third ring. The applied sciences, metallurgy, ceramics, and polymer science are located in the middle ring. Materials science and engineering is shown to form a bridge of materials knowledge from the basic sciences (and mathematics) to the engineering disciplines.

1.3 TYPES OF MATERIALS

For convenience most engineering materials are divided into *three* main or fundamental classes: **metallic materials, polymeric materials,** and **ceramic materials.** In this chapter we shall distinguish among them on the basis of some of their important mechanical, electrical, and physical properties. In subsequent chapters, we shall study the internal structural differences among these types of materials. In addition to the three main classes of materials, we shall consider two processing or applicational classes, **composite materials** and **electronic materials,** because of their great engineering importance.

1.3.1 Metallic Materials

These materials are inorganic substances that are composed of one or more metallic elements and may also contain some nonmetallic elements. Examples of metallic elements are iron, copper, aluminum, nickel, and titanium. Nonmetallic elements such as carbon, nitrogen, and oxygen may also be contained in metallic materials. Metals have a crystalline structure in which the atoms are arranged in an orderly manner. Metals in general are good thermal and electrical conductors. Many metals are relatively strong and ductile at room temperature, and many maintain good strength even at high temperatures.

Metals and alloys[2] are commonly divided into two classes: **ferrous metals and alloys** that contain a large percentage of iron such as the steels and cast irons and **nonferrous metals and alloys** that do not contain iron or contain only a relatively small amount of iron. Examples of nonferrous metals are aluminum, copper, zinc, titanium, and nickel. The distinction between ferrous and nonferrous alloys is made because of the significantly higher usage and production of steels and cast irons when compared to other alloys.

Metals in their alloyed and pure forms are used in numerous industries including aerospace, biomedical, semiconductor, electronic, energy, civil structural, and transport. The U.S. production of basic metals such as aluminum, copper, zinc, and magnesium is expected to follow the U.S. economy fairly closely. However, the production of iron and steel has been less than expected because of global competition and the always-important economical reasons. Materials scientists and engineers are constantly attempting to improve the properties of existing alloys and to design and produce new alloys with improved strength, high temperature strength, creep (see Sec. 7.4), and fatigue (see Sec. 7.2) properties. The existing alloys may be improved by better chemistry, composition control, and processing techniques. For example, by 1961, new and improved nickel-base, iron-nickel-cobalt-base **superalloys** were available for use in high-pressure turbine airfoils in aircraft gas turbines. The term superalloy was used because of their improved performance at elevated temperatures of approximately 540°C (1000°F) and high stress levels. Figures 1.5 and 1.6 show a PW-4000 gas turbine engine that is made primarily of metal alloys and superalloys. The metals used inside the engine must be

---

[2] A metal alloy is a combination of two or more metals or a metal (metals) and a nonmetal (nonmetals).

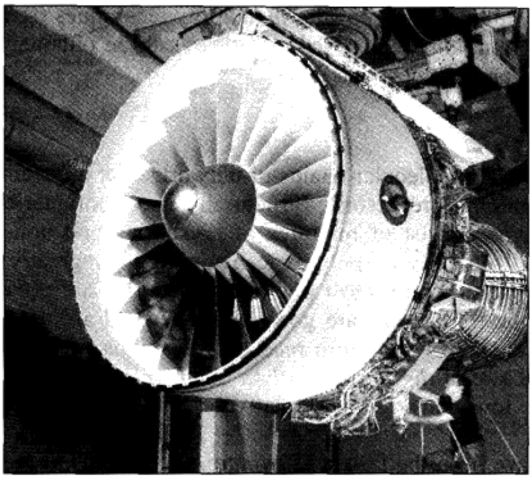


Figure 1.5
The aircraft turbine engine (PW 4000) shown is made principally of metal alloys. The latest high-temperature, heat resistant, high-strength nickel-base alloys are used in this engine. This engine has many advanced, service-proven technologies to enhance operational performance and durability. These include second-generation single-crystal turbine blade materials, powder metal disks, and an improved full authority digital electronic control.
(Courtesy of Pratt & Whitney Co.)

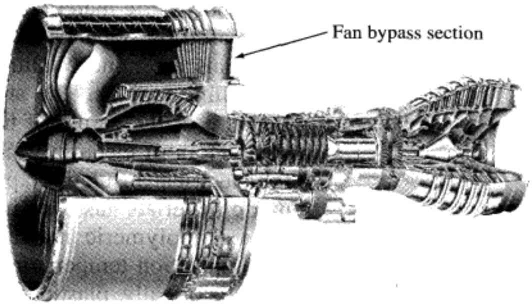


Figure 1.6
Cutaway of the PW 4000 112-in. (284.48 cm) gas turbine engine, showing fan bypass section.
(Courtesy of Pratt & Whitney Co.)

able to withstand high temperatures and pressures generated during its operation. By 1980, casting techniques were improved to produce directionally solidified columnar grain (see Sec. 4.2) and single crystal casting nickel-base alloys (see Sec. 4.2). By the 1990s, single crystal directionally solidified cast alloys were standard in many aircraft gas turbine applications. The better performance of superalloys at elevated operating temperatures, significantly improved the efficiency of the aircraft engines.

Many metal alloys such as titanium alloys, stainless steel, and cobalt-base alloys are also used in biomedical applications, including orthopedic implants, heart valves, fixations devices, and screws. These materials offer high strength, stiffness, and biocompatibility. Biocompatibility is important because the environment inside the human body is extremely corrosive, and therefore materials used for such applications must be effectively impervious to this environment.

In addition to better chemistry and composition control, researchers and engineers also concentrate on improving new processing techniques of these materials. Processes such as hot isostatic pressing (see Sec. 11.4) and isothermal forging have led to improved fatigue life of many alloys. Also, powder metallurgy techniques (see Sec. 11.4) will continue to be important since improved properties can be obtained for some alloys with lower finished product cost.

1.3.2 Polymeric Materials

Most polymeric materials consist of long molecular chains or networks that are usually based on organics (carbon-containing precursors). Structurally, most polymeric materials are noncrystalline, but some consist of mixtures of crystalline and noncrystalline regions. The strength and ductility of polymeric materials vary greatly. Because of the nature of their internal structure, most polymeric materials are poor conductors of electricity. Some of these materials are good insulators and are used for electrical insulative applications. One of the more recent applications of polymeric materials has been in manufacture of *digital video disks* (DVDs) (Fig. 1.7). In general, polymeric materials have low densities and relatively low softening or decomposition temperatures.

Historically, plastic materials have been the fastest growing basic material in the United States, with a growth rate of 9 percent per year on a weight basis (Fig. 1.14). However, the growth rate of plastics through 1995 dropped to below 5 percent, a significant decrease. This drop was expected because plastics have already substituted for metals, glass, and paper in most of the main volume markets, such as packaging and construction, for which plastics are suitable.

Engineering plastics such as nylon are expected to remain competitive with metals, according to some predictions. Figure 1.8 shows expected costs for engineering plastic resins versus some common metals. The polymer-supplying industries are increasingly focusing development of polymer-polymer mixtures, also known as *alloys* or **blends,** to fit specific applications for which no other single polymer is suitable. Because blends are produced based on existing polymers with well-known properties,

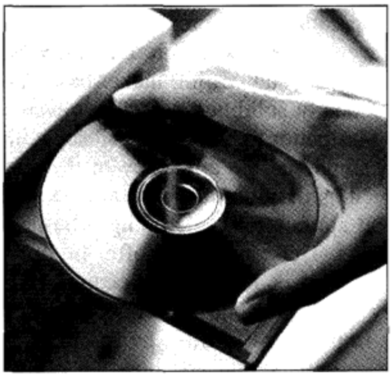


Figure 1.7
Plastic resin producers are developing ultrapure, high-flow grades of polycarbonate plastic for DVDs.
(© *Getty/RF.*)

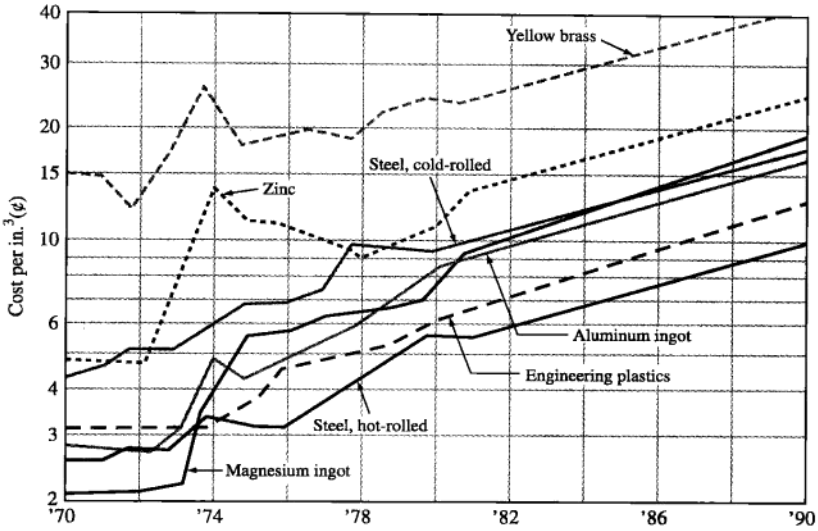
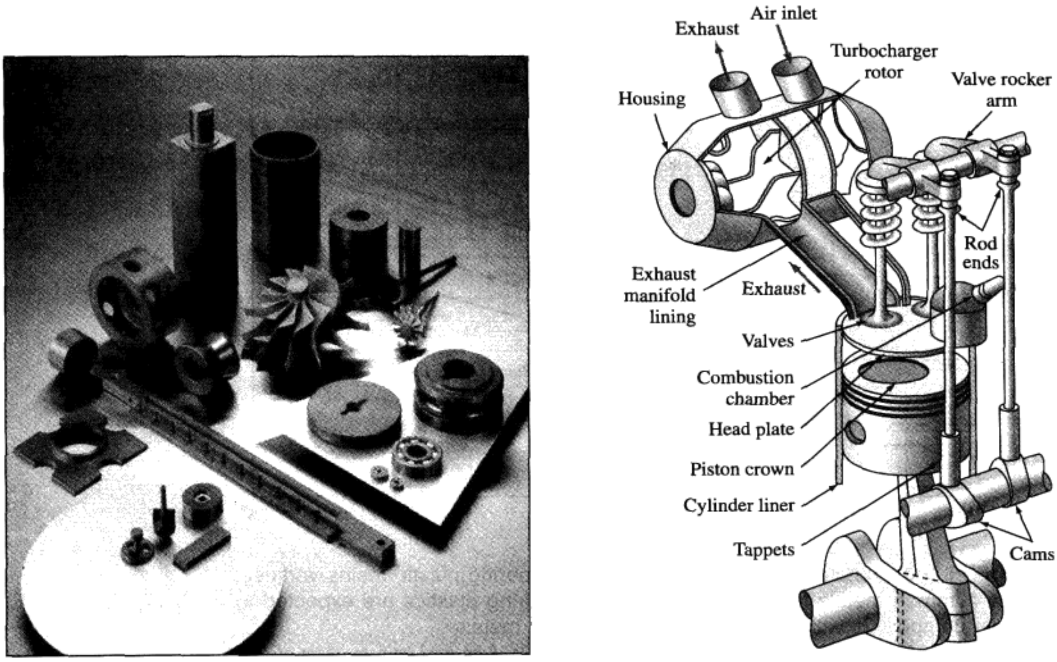


Figure 1.8
Historical and expected competitive costs of engineering plastic resins versus some common metals from 1970 to 1990. Engineering plastics are expected to remain competitive with cold-rolled steel and other metals.
(From Modern Plastics, August 1982, p. 12, and new data, 1998. Reprinted by permission of Modern Plastics.)

their development is less costly and more reliable than synthesizing a new single polymer for a specific application. For example, elastomers (a highly deformable type of polymer) are often blended with other plastics to improve the impact strength of the material. Such blends have important usage in automotive bumpers, power tool housing, sporting goods, and the synthetic components used in many indoor track facilities, which are generally made of a combination of rubber and polyeurathane. Acrylic coatings blended with various fibers and fillers and with brilliant colors are used as coating material for tennis courts and playgrounds. Yet, other polymer-coating materials are being used for protection against corrosion, aggressive chemical environments, thermal shock, impact, wear, and abrasion. Search for new polymers and blends continues because of their low cost and suitable properties for many applications.

1.3.3 Ceramic Materials

Ceramic materials are inorganic materials that consist of metallic and nonmetallic elements chemically bonded together. Ceramic materials can be crystalline, noncrystalline, or mixtures of both. Most ceramic materials have high-hardness and high-temperature strength but tend to be brittle (little or no deformation prior to fracture). Advantages of ceramic materials for engineering applications include light weight, high strength and hardness, good heat and wear resistance, reduced friction, and insulative properties (Figs. 1.9 and 1.10). The insulative property along with high heat and wear resistance of many ceramics make them useful for furnace linings for heat treatment and melting



(*a*) (*b*)

Figure 1.9
(*a*) Examples of a newly developed generation of engineered ceramic materials for advanced engine applications. The black items include engine valves, valve seat inserts, and piston pins made of silicon nitride. The white item is a port-manifold liner made of an alumina ceramic material.
(*Courtesy of Kyocera Industrial Ceramics Corp.*)
(*b*) Potential ceramic component applications in a turbocharged diesel engine.
(*After Metals and Materials, December 1988.*)

of metals such as steel. The search for new plastics and alloys continues because of their lower cost and suitable properties for many applications.

The historic rate of growth of traditional ceramic materials such as clay, glass, and stone in the United States has been 3.6 percent (1966 to 1980). The expected growth rate of these materials from 1982 to 1995 followed the U.S. economy. In the past few decades, an entirely new family of ceramics of oxides, nitrides, and carbides, with improved properties, have been produced. The new generation of ceramic materials called *engineering ceramics, structural ceramics,* or **advanced ceramics** has higher strength, better wear and corrosion resistance (even at higher temperatures), and enhanced thermal shock (due to sudden exposure to very high or very low temperatures) resistance. Among the established advanced ceramic materials are alumina (oxide), silicon nitride (nitride), and silicon carbide (carbide).

An important aerospace application for advanced ceramics is the use of ceramic tiles for the space shuttle. The ceramic tiles are made of silicon carbide because of its ability to act as a heat shield and to quickly return to normal temperatures upon

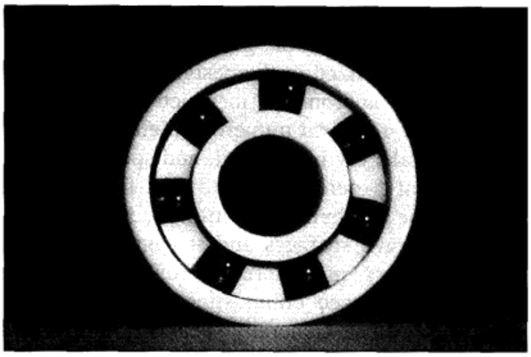


Figure 1.10
High-performance ceramic ball bearings and races are made from titanium and carbon nitride feedstocks through power metal technology.
(© *David A. Tietz/Editorial Image, LLC.*)

removal of the heat source. These ceramic materials thermally protect the aluminum internal substructure of the space shuttle during ascent and reentry into the earth's atmosphere (see Figs. 11.43 and 11.44). Another application for advanced ceramics that points to the versatility, importance, and future growth of this class of materials is its use as a cutting tool material. For instance, silicon nitride with a high thermal shock resistance and fracture toughness is an excellent cutting tool material.

The applications for ceramic materials are truly unlimited as they can be applied to aerospace, metal manufacturing, biomedical, automobile, and numerous other industries. The two main drawbacks for this class of materials are that they are (1) difficult to process into finished products and are therefore expensive and (2) brittle and have low fracture toughness compared to metals. If techniques for developing high toughness ceramics are developed further, these materials could show a tremendous upsurge for engineering applications.

1.3.4 Composite Materials

A composite material may be defined as two or more materials (phases or constituents) integrated to form a new one. The constituents keep their properties, and the overall composite will have properties different than each of them. Most composite materials consist of a selected filler or reinforcing material and a compatible resin binder to obtain the specific characteristics and properties desired. Usually, the components do not dissolve in each other, and they can be physically identified by an interface between them. Composites can be of many types. Some of the predominant types are fibrous (composed of fibers in a matrix) and particulate (composed of particles in a matrix). Many different combinations of reinforcements and matrix materials are used to produce composite materials. For example, the matrix material may be a metal such as aluminum, a ceramic such as alumina, or a polymer such as epoxy. Depending on the type of matrix used, the composite may be classified as a *metal matrix composite* (MMC), *ceramic matrix composite* (CMC), or a *polymer matrix composite* (PMC). The fiber or particulate materials may also be selected from any of the three main classes of materials with examples such as carbon, glass, aramid, silicon carbide, and others. The combinations of materials utilized in the design of composites depend mainly on the type of application and the environment in which the material will be used.

Composite materials have replaced numerous metallic components especially in aerospace, avionics, automobile, civil structural, and sports equipment industries. An average annual gain of about 5 percent is predicted for the future usage of these materials. One reason is due to their high strength and stiffness-to-weight ratio. Some advanced composites have stiffness and strength similar to some metals but with significantly lower density, and therefore lower overall component weight. These characteristics make advanced composites extremely attractive in situations where component weight is critical. Generally speaking, similar to ceramic materials, the main disadvantage of most composite materials is their brittleness and low fracture toughness. Some of these shortcomings may be improved, in certain situations, by the proper selection of the matrix material.

Two outstanding types of *modern composite materials* used for engineering applications are fiberglass-reinforcing material in a polyester or epoxy matrix and carbon fibers in an epoxy matrix. Figure 1.11 shows schematically where carbon-fiber-epoxy composite material was used for the wings and engines of the C-17 transport plane. Since these airplanes have been constructed, new cost-saving procedures and modifications have been introduced (See *Aviation Week & Space Technology*, June 9, 1997, p. 30).

1.3.5 Electronic Materials

Electronic materials are not a major type of material by production volume but are an extremely important type of material for advanced engineering technology. The most important electronic material is pure silicon that is modified in various ways to change

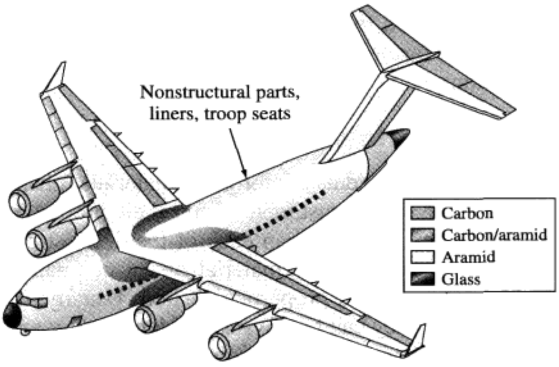


Figure 1.11
Overview of the wide variety of composite parts used in the Air Force's C-17 transport. This airplane has a wingspan of 165 ft and uses 15,000 lb of advanced composites.
(From Advanced Composites, May/June 1988, p. 53.)

its electrical characteristics. A multitude of complex electronic circuits can be miniaturized on a silicon chip that is about 3/4 in. square (1.90 cm square) (Fig. 1.12). Microelectronic devices have made possible such new products as communication satellites, advanced computers, handheld calculators, digital watches, and robots (Fig. 1.13).

The use of silicon and other semiconductor materials in solid-state and microelectronics has shown a tremendous growth since 1970, and this growth pattern is expected to continue. The impact of computers and other industrial types of equipment using integrated circuits made from silicon chips has been spectacular. The full effect of computerized robots in modern manufacturing is yet to be determined. Electronic materials will undoubtedly play a vital role in the "factories of the future" in which almost all manufacturing may be done by robots assisted by computer-controlled machine tools.

Over the years integrated circuits have been made with a greater and greater density of transistors located on a single silicon chip with a corresponding decrease in transistor width. For example, in 1998 the point-to-point resolution for the smallest measurement on a silicon chip was 0.18 μm and the diameter of the silicon wafer used was 12 in. (300 mm). Another improvement may be the replacement of aluminum by copper for interconnects because of the higher conductivity of copper.

1.4 COMPETITION AMONG MATERIALS

Materials compete with each other for existing and new markets. Over a period of time many factors arise that make it possible for one material to replace another for certain applications. Certainly cost is a factor. If a breakthrough is made in the processing of a certain type of material so that its cost is decreased substantially, this material may replace another for some applications. Another factor that causes material replacement changes is the development of a new material with special properties for some applications. As a result, over a period of time, the usage of different materials changes.

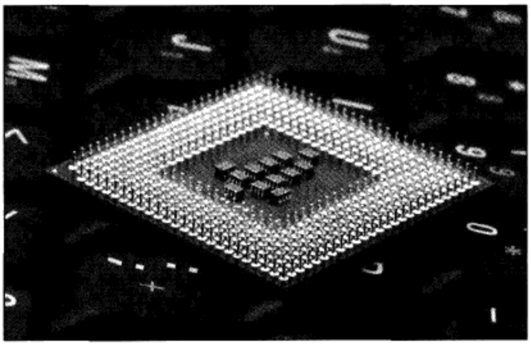


Figure 1.12
Modern microprocessors have a multitude of outlets, as indicated on this picture of Intel's Pentium II microprocessor.
(© *IMP/Alamy RF.*)

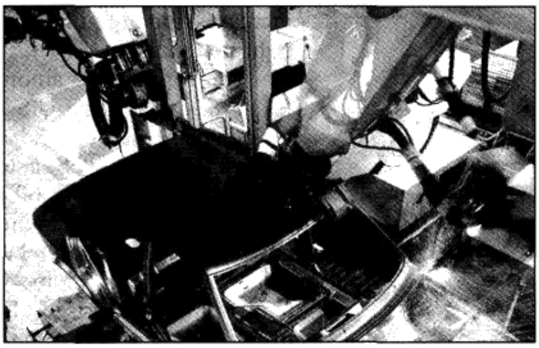


Figure 1.13
Robotic arms wielding car parts.
(*CORBIS/RF.*)

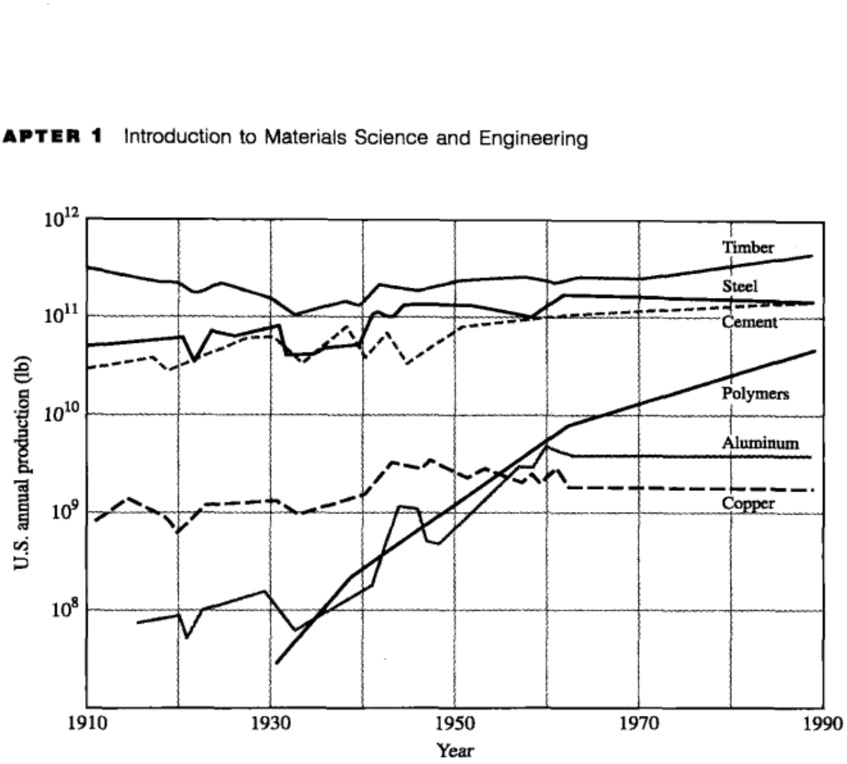


Figure 1.14
Competition of six major materials produced in the United States on a weight (pound) basis. The rapid rise in the production of aluminum and polymers (plastics) is evident.
(From J.G. Simon, Adv. Mat. & Proc., 133:63 (1988) and new data. Used by permission of ASM International.)

Figure 1.14 shows graphically how the production of six materials in the United States on a weight basis varied over the past years. Aluminum and polymers show an outstanding increase in production since 1930. On a volume basis the production increases for aluminum and polymers are even more accentuated since these are light materials.

The competition among materials is evident in the composition of the U.S. auto. In 1978, the average U.S. auto weighed 4000 lb (1800 kg) and consisted of about 60 percent cast iron and steel, 10 to 20 percent plastics, and 3 to 5 percent aluminum. The 1985 U.S. auto by comparison weighed an average of 3100 lb (1400 kg) and consisted of 50 to 60 percent cast iron and steel, 10 to 20 percent plastics, and 5 to 10 percent aluminum. Thus, in the period 1978–1985 the percentage of steel declined, that of polymers increased, and that of aluminum remained about the same. In 1997 the domestic U.S. auto weighed an average of 3248 lb (1476 kg), and plastics comprised about 7.4 percent of it (Fig. 1.15). The trend in the usage of materials appears to be more aluminum and steel in autos and less *cast* iron. The amount of plastics (by percentage) in autos appears to be about the same (Fig. 1.16).

For some applications only certain materials can meet the engineering requirements for a design, and these materials may be relatively expensive. For example, the modern jet engine (Fig. 1.5) requires high-temperature nickel-base superalloys to function. These materials are expensive, and no cheap substitute has been found to replace them. Thus, although cost is an important factor in engineering design, the materials used must also meet performance specifications. Replacement of one material by another will continue in the future since new materials are being discovered and new processes are being developed.

1.5 RECENT ADVANCES IN MATERIALS SCIENCE AND TECHNOLOGY AND FUTURE TRENDS

In recent decades, a number of exciting initiatives in materials science have been undertaken that could potentially revolutionize the future of the field. Smart materials (devices at micrometer size scale) and nanomaterials are two categories of materials that will critically affect all major industries.

1.5.1 Smart Materials

Some smart materials have been around for years but are finding more applications. They have the ability to sense external environmental stimuli (temperature, stress, light, humidity, and electric and magnetic fields) and respond to them by changing their properties (mechanical, electrical, or appearance), structure, or functions. These materials are generically called **smart materials.** Smart materials or systems that use smart materials consist of sensors and actuators. The sensory component detects a change in the environment, and the actuator component performs a specific function or a response. For instance, some smart materials change or produce color when exposed to changes in temperature, light intensity, or an electric current.

Some of the more technologically important smart materials that can function as actuators are **shape-memory alloys** and **piezoelectric** ceramics. Shape-memory alloys are metal alloys that, once strained, revert back to their original shape upon an increase in temperature above a critical transformation temperature. The change in shape back to the original is due to a change in the crystal structure above the transformation temperature. One biomedical application of a shape-memory alloys

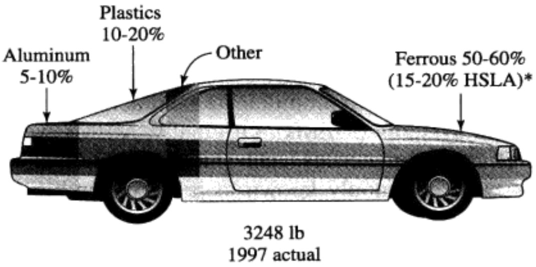


Figure 1.15
Breakdown of weight percentages of major materials used in the average 1985 U.S. automobile.
**HSLA—High Strength Low Alloy Steel*

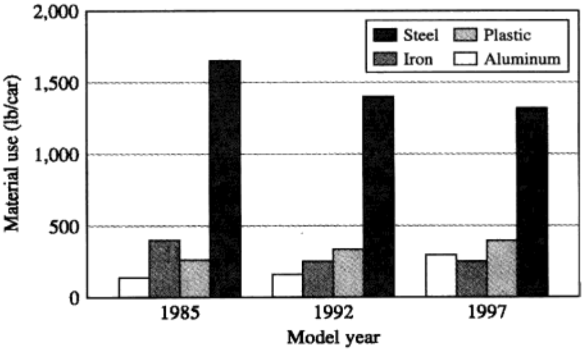
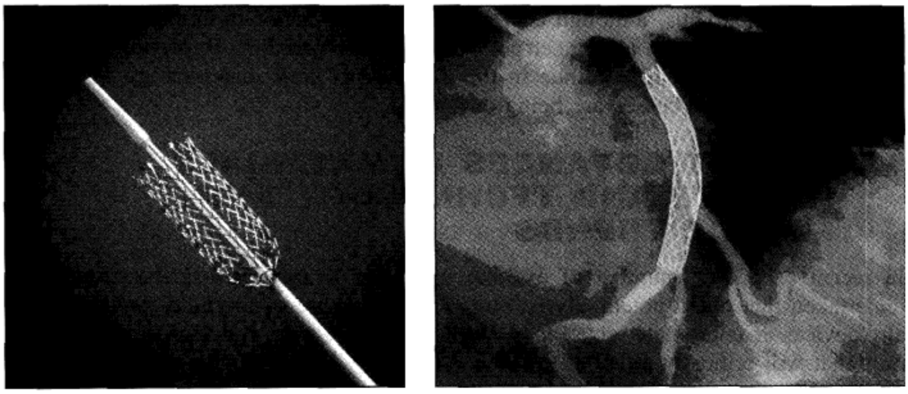


Figure 1.16
Predictions and use of materials in U.S. automobile.
(After J.G. Simon, Adv. Mat. & Proc., 133:63(1997) and new data.)



(*a*) (*b*)

Figure 1.17
Shape-memory alloys used as a stent to expand narrowed arteries or support weakened ones: (*a*) stent on a probe and (*b*) stent positioned in a damaged artery for support.
(Source: *http://www.designinsite.dk/htmsider/inspmat.htm.*)
(*Courtesy of Nitinol Devices & Components © Sovereign/Phototake NYC.*)

is as a stent for supporting weakened artery walls or for expanding narrowed arteries (Fig. 1.17). The deformed stent is first delivered in the appropriate position in the artery using a probe Fig. 1.17*a*. The stent expands to its original shape and size after increasing its temperature to body temperature Fig. 1.17*b*. For comparison, the conventional method of expanding or supporting an artery is through the use of a stainless steel tube that is expanded using a balloon. Examples of shape-memory alloys are nickel-titanium and copper-zinc-aluminum alloys.

Actuators may also be made of piezoelectric materials. The materials produce an electric field when exposed to a mechanical force. Conversely, a change in an external electric field will produce a mechanical response in the same material. Such materials may be used to sense and reduce undesirable vibrations of a component through their actuator response. Once a vibration is detected, a current is applied to produce a mechanical response that counters the effect of the vibration.

Now let us consider the design and development of systems at micrometer size scale that use smart materials and devices to sense, communicate, and actuate: such is the world of **microelectromechanical systems** (MEMs). Originally, MEMs were devices that integrated technology, electronic materials, and smart materials on a semiconductor chip to produce what were commonly known as a **micromachines.** The original MEMs device had the microscopic mechanical elements fabricated on silicon chips using integrated circuits technology; MEMs were used as sensors or actuators. But today the term "MEMs" is extended to any miniaturized device. The applications of MEMs are also numerous, including but not limited to micropumps, locking systems, motors, mirrors, and sensors. For instance, MEMs are used in automobile airbags to sense both the deceleration and the size of the person sitting in the car and to deploy the airbag at a proper speed.

1.5.2 Nanomaterials

Nanomaterials are generally defined as those materials that have a characteristic length scale (that is, particle diameter, grain size, layer thickness, etc.) smaller than 100 nm ($1 \text{ nm} = 10^{-9}$ m). Nanomaterials can be metallic, polymeric, ceramic, electronic, or composite. In this respect, ceramic powder aggregates of less than 100 nm in size, bulk metals with grain size less than 100 nm, thin polymeric films with thickness less than 100 nm, and electronic wires with diameter less than 100 nm are all considered nanomaterials or nanostructured materials. At the nanoscale, the properties of the material are neither that of the molecular or atomic level nor that of the bulk material. Although a tremendous amount of research and development activities has been devoted to this topic in the past decade, early research on nanomaterials dates back to the 1960s when chemical flame furnaces were used to produce particles smaller than one micron ($1 \text{ micron} = 10^{-6} \text{ m} = 10^3$ nm) in size. The early applications of nanomaterials were as chemical catalysts and pigments. Metallurgists have always been aware that by refining the grain structure of a metal to ultrafine (submicron) levels, its strength and hardness increases significantly in comparison to the coarse-grained (micron-size) bulk metal. For example, nanostructured pure copper has a yield strength six times that of coarse-grained copper.

The reasons for the recent extraordinary attention to these materials may be due to the development of (1) new tools that make the observation and characterization of these materials possible and (2) new methods of processing and synthesizing nanostructured materials that enable researchers to produce these materials more easily and at a higher yield rate.

The future applications of nanomaterials are only limited to the imagination, and one of the major obstacles in fulfilling this potential is the ability to efficiently and inexpensively produce these materials. Consider the manufacturing of orthopedic and dental implants from nanomaterials with better biocompatibility characteristics, better strength, and better wear characteristics than metals. One such material is nanocrystalline zirconia (zirconium oxide), a hard and wear resistant ceramic that is chemically stable and biocompatible. This material can be processed in a porous form, and when it is used as implant material, it allows for bone to grow into its pores, resulting in a more stable fixation. The metal alloys that are currently used for this application do not allow for such interaction and often loosen over time, requiring further surgery. Nanomaterials may also be used in producing paint or coating materials that are significantly more resistant to scratching and environmental damage. Also, electronic devices such as transistors, diodes, and even lasers may be developed on a nanowire. Such materials science advancements will have both technological and economical impact on all areas of engineering and industries.

Welcome to the fascinating and exceedingly interesting world of materials science and engineering!

1.6 DESIGN AND SELECTION

Material engineers should be knowledgeable of various classes of materials, their properties, structure, manufacturing processes involved, environmental issues, economic issues, and more. As the complexity of the component under consideration increases, the complexity of the analysis and the factors involved in the materials selection process also increase. Consider the materials selection issues for the frame and forks of a bicycle. The selected material must be strong enough to support the load without yielding (permanent deformation) or fracture. The chosen material must be stiff to resist excessive elastic deformation and fatigue failure (due to repeated loading). The corrosion resistance of the material may be a consideration over the life of the bicycle. Also, the weight of frame is important if the bicycle is used for racing: It must be lightweight. What materials will satisfy all of the above requirements? A proper materials selection process must consider the issues of strength, stiffness, weight, and shape of the component (shape factor) and utilize materials selection charts in order to determine the most suitable material for the application. The detailed selection process is outside the scope of this textbook, but we use this example as an exercise in identifying various material candidates for this application. It turns out that a number of materials may satisfy the strength, stiffness, and weight considerations including some aluminum alloys, titanium alloys, magnesium alloys, steel, carbon fiber reinforced plastic (CFRP), and even wood. Wood has excellent properties for our application but it cannot be easily shaped to form a frame and the forks. Further analysis shows CFRP is the best choice; it offers a strong, stiff, and lightweight frame that is both fatigue and corrosion resistant. However, the fabrication process is costly. Therefore, if cost is an issue, this material may not be the most suitable choice. The remaining materials, all metal alloys, are all suitable and comparatively easy to manufacture into the desired shape. If cost is a major issue, steel emerges as the most suitable choice. On the other hand, if lower bicycle weight is important, the aluminum alloy emerge as the most suitable material. Titanium and magnesium alloys are more expensive than both aluminum and steel alloys and are lighter than steel; they, however, do not offer significant advantages over aluminum.

1.7 SUMMARY

Materials science and materials engineering (collectively, materials science and engineering) form a bridge of materials knowledge between the basic sciences (and mathematics) and the engineering disciplines. Materials science is concerned primarily with the search for basic knowledge about materials, whereas materials engineering is concerned mainly with using applied knowledge about materials.

The three main types of materials are metallic, polymeric, and ceramic materials. Two other types of materials that are very important for modern engineering technology are composite and electronic materials. All these types of materials will be dealt with in this book. Smart materials and devices in micrometer size scale and nanomaterials are presented as new classes of materials with novel and important applications in many industries.

Materials compete with each other for existing and new markets, and so the replacement of one material by another for some applications occurs. The availability of raw materials, cost of manufacturing, and the development of new materials and processes for products are major factors that cause changes in materials usage.

1.8 DEFINITIONS

Sec. 1.1

Materials: substances of which something is composed or made. The term *engineering materials* is sometimes used to refer specifically to materials used to produce technical products. However, there is no clear demarcation line between the two terms, and they are used interchangeably.

Sec. 1.2

Materials science: a scientific discipline that is primarily concerned with the search for basic knowledge about the internal structure, properties, and processing of materials.

Materials engineering: an engineering discipline that is primarily concerned with the use of fundamental and applied knowledge of materials so that they can be converted into products needed or desired by society.

Sec. 1.3

Metallic materials (metals and metal alloys): inorganic materials that are characterized by high thermal and electrical conductivities. Examples are iron, steel, aluminum, and copper.

Polymeric materials: materials consisting of long molecular chains or networks of low-weight elements such as carbon, hydrogen, oxygen, and nitrogen. Most polymeric materials have low electrical conductivities. Examples are polyethylene and *polyvinyl chloride* (PVC).

Ceramic materials: materials consisting of compounds of metals and nonmetals. Ceramic materials are usually hard and brittle. Examples are clay products, glass, and pure aluminum oxide that has been compacted and densified.

Composite materials: materials that are mixtures of two or more materials. Examples are fiberglass-reinforcing material in a polyester or epoxy matrix.

Electronic materials: materials used in electronics, especially microelectronics. Examples are silicon and gallium arsenide.

Ferrous metals and alloys: metals and alloys that contain a large percentage of iron such as steels and cast irons.

Nonferrous metals and alloys: metals and alloys that do not contain iron, or if they do contain iron, it is only in a relatively small percentage. Examples of nonferrous metals are aluminum, copper, zinc, titanium, and nickel.

Superalloys: metal alloys with improved performance at elevated temperatures and high stress levels.

Blends: mixture of two or more polymers, also called polymer alloys.

Advanced ceramics: new generation of ceramics with improved strength, corrosion resistance, and thermal shock properties; also called engineering or structural ceramics.

Sec. 1.5

Smart materials: materials with the ability to sense and respond to external stimuli.

Shape-memory alloys: materials that can be deformed but return to their original shape upon an increase in temperature.

Piezoelectric ceramics: materials that produce an electric field when subjected to mechanical force (and vice versa).

Microelectromechanical systems (MEMs): any miniaturized device that performs sensing and/or actuating function.

Micromachine: MEMs that perform a specific function or task.

Nanomaterials: materials with a characteristic length scale smaller than 100 nm.

1.9 PROBLEMS

Knowledge and Comprehension Problems

1.1 What are materials? List eight commonly encountered engineering materials.

1.2 What are the main classes of engineering materials?

1.3 What are some of the important properties of each of the five main classes of engineering materials?

1.4 Define a composite material. Give an example of a composite material.

1.5 Provide a list of characteristics for structural materials to be used in space applications.

1.6 Define smart materials. Give an example of such material and an application for it.

1.7 What are MEMs? Give an application for MEMs.

1.8 What are nanomaterials? What are some proposed advantages of using nanomaterials over their conventional counterparts?

1.9 Nickel-base superalloys are used in the structure of aircraft turbine engines. What are the major properties of this metal that make it suitable for this application?

1.10 Make a list of items that you find in your kitchen (at least 15 items). In each item, determine the class of materials (identify the specific material if you can) used in the structure of the item.

1.11 Make a list of all the major components of your school's varsity basketball court. For each major component, determine the class of materials used in its structure (identify the specific materials if you can).

1.12 Make a list of major components in your automobile (at least 15 components). For each component, determine the class of materials used in its structure (identify the specific material if you can).

1.13 Make a list of major components in your computer (at least 10 components). For each component, determine the class of materials used in its structure (identify the specific material if you can).

1.14 Make a list of major components in your classroom including the constructional elements (at least 10 components). For each component, determine the class of materials used in its structure (identify the specific material if you can).

Application and Analysis Problems

1.15 List some materials usage changes that you have observed over a period of time in some manufactured products. What reasons can you give for the changes that have occured?

1.16 (*a*) What kind of material is OFHC copper? (*b*) What are the desirable properties of OFHC copper? (*c*) What are the applications of OFHC copper in the power industry?

1.17 (*a*) To which class of materials does PTFE belong? (*b*) What are its desirable properties? (*c*) What are its applications in cookware manufacturing industries?

1.18 Why should civil engineers be knowledgeable about composition, properties, and processing of materials?

1.19 Why should mechanical engineers be knowledgeable about composition, properties, and processing of materials?

1.20 Why should chemical engineers be knowledgeable about composition, properties, and processing of materials?

1.21 Why should industrial engineers be knowledgeable about composition, properties, and processing of materials?

1.22 Why should petroleum engineers be knowledgeable about composition, properties, and processing of materials?

1.23 Why should electrical engineers be knowledgeable about composition, properties, and processing of materials?

1.24 Why should biomedical engineers be knowledgeable about composition, properties, and processing of materials?

Synthesis and Evaluation Problems

1.25 What factors might cause materials usage predictions to be incorrect?

1.26 Consider the common household component in a lightbulb: (*a*) identify various critical components of this item, (*b*) determine the material selected for each critical component, and (*c*) design a process that would be used to assemble the lightbulb.

1.27 (*a*) Name the important factors in selecting materials for the frame of a mountain bike. (*b*) Steel, aluminum, and titanium alloys have all been used as the primary metals in the structure of a bicycle; determine the major weaknesses and strengths of each. (*c*) The more-modern bikes are made of advanced composites. Explain why, and name a specific composite used in the structure of a bike.

1.28 (*a*) Name the important criteria for selecting materials to use in a protective sports helmet. (*b*) Identify materials that would satisfy these criteria. (*c*) Why would a solid metal helmet not be a good choice?

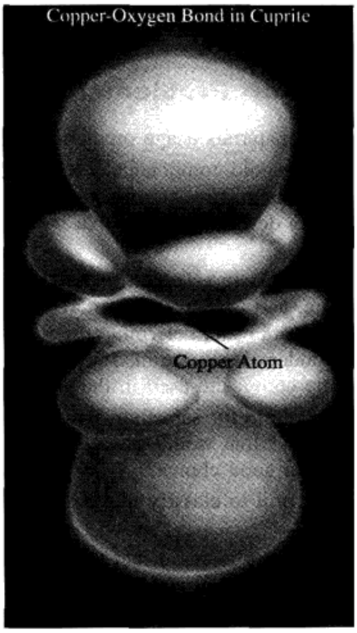
1.29 Why is it important or helpful to classify materials into different groups as we have done in this chapter?

1.30 A certain application requires a material that must be very hard and corrosion resistant at room temperature and atmosphere. It would be beneficial, but not necessary, if the material were also impact resistant. (*a*) If you only consider the major requirements, which classes of materials would you search for this selection? (*b*) If you consider both major and minor requirements, which classes would you search? (*c*) Suggest a material.

1.31 Give as many examples as you can on how materials science and engineering is important to the ice climber in the cover image.

CHAPTER 2

Atomic Structure and Bonding



(*© Tom Pantages adaptation/courtesy Prof. J. Spence.*)

Atomic orbitals represent the statistical likelihood that electrons will occupy various points in space. Except for the innermost electrons of the atoms, the shapes of the orbitals are nonspherical. Until recently, we have only been able to imagine the existence and shape of these orbitals because no experimental verifications were available. Recently, scientists have been able to create a three-dimensional image of these orbitals using a combination of X-ray diffraction and electron microscopy techniques. The chapter-opening image shows the orbital of d state electrons of the copper-oxygen bond in Cu_2O. Through an understanding of the bonding in copper oxides, using the techniques just described, researchers edge closer to explaining the nature of high-temperature superconductivity in copper oxides.[1] ■

---

[1] www.aip.org/physnews/graphics/html/orbital.html

LEARNING OBJECTIVES

By the end of this chapter, students will be able to . . .

1. Describe the nature and structure of an atom as well as its electronic structure.
2. Describe various types of primary bonds including ionic, covalent and metallic.
3. Describe covalent bonding by carbon.
4. Describe various types of secondary bonds and differentiate between these and primary bonds.
5. Describe the effect of bond type and strength on the mechanical and electrical performance of various classes of materials.
6. Describe mixed bonding in materials.

2.1 ATOMIC STRUCTURE AND SUBATOMIC PARTICLES

In the fifth century BC, the Greek philosopher Democritus[2] postulated that matter ultimately consists of small indivisible particles which he called *atomos* (or *atoms*) meaning uncuttable or indivisible. This idea was lost on the scientific community until the seventeenth century when Robert Boyle[3] asserted that elements are made up of "simple bodies" that themselves are not made up of any other bodies; a description of the atom very similar to that of Democritus some 2200 years prior. In the early nineteenth century, atomism was reborn as John Dalton[4] hypothesized the most precise definition of the building blocks of matter by stating that matter is made up of small particles called *atoms* and that all atoms in a pure substance are identical having the same size, shape, mass, and chemical properties. Furthermore, he hypothesized that the atoms of one pure substance are different from the atoms of other pure substances and when combined, in specific simple fractions, form different compounds—**law of multiple proportions.** Finally, he proposed that a chemical reaction is explained by separation, combination, or rearrangement of atoms and that a chemical reaction does not lead to creation or destruction of matter—**law of mass conservation.** Dalton's and Boyle's assertions ignited a revolution in the field of chemistry.

---

[2] Democritus (460 BC–370 BC). Greek materialist philosopher with contributions to the fields of mathematics, minerals and plants, astronomy, epistemology, and ethics.

[3] Robert Boyle (1627–1691). Irish philosopher, chemist, physicist, and inventor best known for the formulation of Boyle's law (studied in physics and thermodynamics).

[4] John Dalton (1766–1844). English chemist, meteorologist, and physicist.

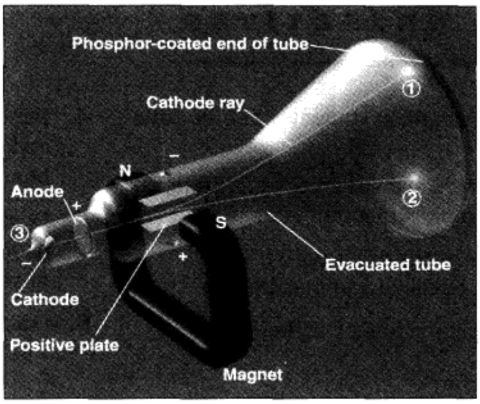


Figure 2.1
A cathode ray tube, consisting of a glass tube, cathode, anode, deflecting plates, and a flourescence screen.

In the late nineteenth century, Henri Becquerel[5] and Marie[6] and Pierre Curie[7] in France, introduced the concept of radioactivity. They suggested that atoms of newly found elements such as polonium and radium spontaneously emit rays and named this phenomenon *radioactivity*. The radiation was shown to consist of α (alpha), β (beta), and γ (gamma) rays. It was also shown that α and β particles have both charge and mass while γ particles have no detectable mass or charge. The major conclusion from these findings was that atoms must be made up of smaller constituents or subatomic particles.

Cathode ray tube experiments were instrumental in identifying one of the constituents or subatomic particles of the atom (Fig. 2.1). A cathode ray consists of a glass tube with air extracted from it. At one end of this tube, two metal plates are connected to a high voltage source. The negatively charged plate (cathode) emits an invisible ray that is attracted by the positively charged plate (anode). The invisible ray is called a *cathode ray*; it consists of negatively charged particles and comes directly from the atoms in the cathode. A hole at the center of the anode allows passage to the invisible ray that continues to travel to the end of the tube where it strikes a specially coated plate (fluorescence screen) and produces tiny flashes, (Fig. 2.1). In a series of such experiments, Joseph J. Thompson[8] concluded that atoms in all matters are made of smaller particles that are negatively charged, called *electrons*. He also calculated the ratio of mass to charge of these electrons to be 5.60×10^{-19} g/C where *Coulomb*, C, is the unit of electrical charge. Later, Robert Millikan,[9] in his oil-drop experiments, determined the fundamental quantity of charge or the charge of an electron (regardless of the source) to be 1.60×10^{-19} C. For an electron, this quantity of charge is represented by -1. Using the ratio of mass to charge of the electron measured by Thompson and the charge of the electron measured by Millikan, the mass of an electron was determined to be 8.96×10^{-28} g. Based on this evidence of the existence of negatively charged electrons, it was deducted that the atom must also contain an equal number of positively charged subatomic particles to maintain its electrical neutrality.

---

[5] Henri Becquerel (1852–1908). French physicist and Nobel laureate (1903).

[6] Marie Curie (1867–1934). Polish (French citizenship) physicist and chemist and Nobel laureate (1903).

[7] Pierre Curie (1859–1906). French physicist and Nobel laureate (1903); shared with Marie Curie and Henri Becquerel.

[8] Joseph J. Thompson (1856–1940). British physicist and Nobel laureate.

[9] Robert Millikan (1868–1953). American physicist (first PhD in physics from Columbia University) and Nobel laureate (1923).

In 1910, Ernest Rutherford,[10] Sir Thompson's student, bombarded a very thin foil of gold with positively charged α particles. He noticed that many of the α particles passed through the foil without deflection, some were slightly deflected, and a few were either largely deflected or completely bounced back. He concluded that (1) most of the atom must be made up of empty space (thus, most particles pass through without deflection) and (2) a small neighborhood at the center of the atom, the nucleus, houses positively charged particles of its own. He suggested that those α particles that deflected intensely or bounced back must have interacted closely with the positively charged nucleus of the atom. The positively charged particles in the nucleus were called *protons*. It was later determined that the proton carries the same quantity of charge as an electron but opposite in sign and has a mass of 1.672×10^{-24} g (1840 times the mass of the electron). For a proton this quantity of charge is represented by $+1$.

Finally, since atoms are electrically neutral, they must have an equal number of electrons and protons. However, neutral atoms have a mass that is larger than the mass of protons alone. In 1932, James Chadwick[11] provided the first evidence of an isolated neutron outside the atom. These particles with no electrical charge and with a mass of 1.674×10^{-24} g (slightly larger than a proton) were called *neutrons*. The mass, charge, and charge unit of the electrons, protons, and neutrons are presented in Table 2.1.

According to an atomic model, a typical atomic radius was about 100 *picometer* (1 picometer $= 1 \times 10^{-12}$ m) with a much smaller nucleus of 5×10^{-3} picometer. If one enlarges an atom to the size of a football stadium, the corresponding nucleus would be the size of a marble. The electrons were thought to be dispersed at some distance from the nucleus in what was called the *charge cloud*. This atomic model and the corresponding dimensions are schematically presented in Fig. 2.2.

When studying the interaction of atoms (similar or different atoms), the electron configuration of each atom is of critical importance. The electrons (especially the ones with the highest energy) determine the extent of reactivity or the tendency of an atom to bond with another.

Table 2.1 Mass, charge, and charge unit of protons, neutrons, and electrons

Particle	Mass (g)	Charge	
		Coulomb (C)	Charge unit
Electron	9.10939×10^{-28}	-1.06022×10^{-19}	-1
Proton	1.67262×10^{-24}	$+1.06022 \times 10^{-19}$	$+1$
Neutron	1.67493×10^{-24}	0	0

---

[10] Ernest Rutherford (1871–1937). Physicist from New Zealand and Nobel laureate (1908).

[11] James Chadwick (1891–1974). English physicist and Nobel laureate (1935).

2.2 ATOMIC NUMBERS, MASS NUMBERS, AND ATOMIC MASSES

2.2.1 Atomic Numbers and Mass Numbers

In the early twentieth century, it was discovered that each atom has a specific number of protons in its nucleus; this number was named the **atomic number** (Z). Each element has its own characteristic atomic number that defines that element. For instance any atom with 6 protons is by definition a carbon atom. In a neutral atom, the atomic number or the number of protons is also equal to the number of electrons in its charge cloud.

The mass of an atom, *atomic mass*, is expressed in **atomic mass units** (amu). One amu is defined as exactly 1/12th the mass of a carbon atom with 6 protons and 6 neutrons. This also indicates that the mass of one neutron or one proton is very close to 1 amu. Thus, a carbon-12 atom itself has an atomic mass of 12 amu.

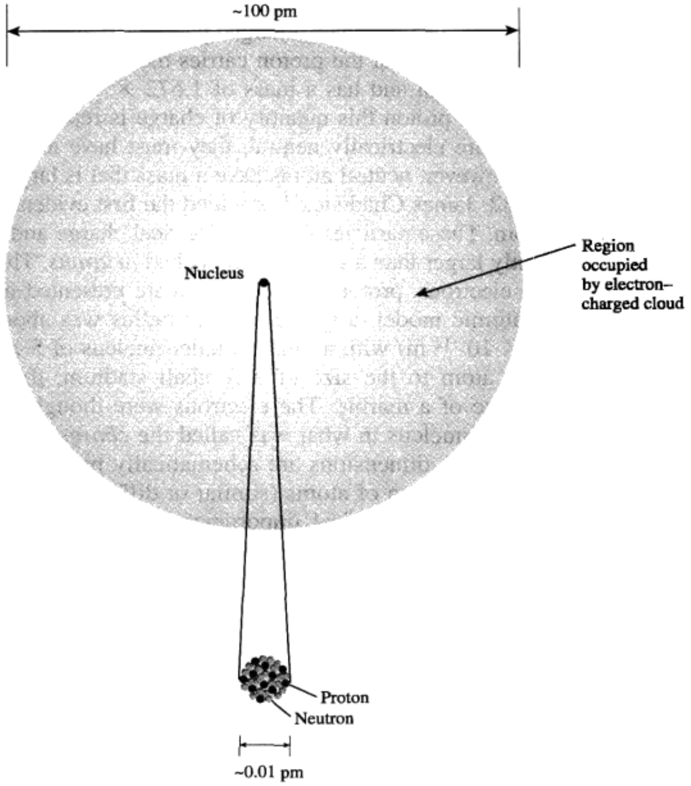


Figure 2.2
The relative size of an atom and its nucleus that is made up of protons and neutrons. Note that contrary to the schematic, the atom boundaries are not well-defined.

The **mass number** (A) is the sum of protons and neutrons in a nucleus of an atom. Except for hydrogen, which does not have a neutron in its most common form, all nuclei contain both protons and neutrons. For instance the carbon atom has a mass number of 12 (6 protons + 6 neutrons). The proper way of expressing both the mass number (A) and the atomic number (Z) of an atom, exemplified here with a carbon atom, is

$${}^{A}_{Z}\mathrm{C} \text{ or } {}^{12}_{6}\mathrm{C}$$

The Z number is redundant; by definition we know the number of protons from the identity of the atom so that often the presentation ${}^{12}\mathrm{C}$ (or carbon-12) is considered sufficient. For example, if we want to find the number of neutrons in iodine-131 (${}^{131}\mathrm{I}$), we see from the periodic table that I is the fifty-third element (53 protons). We can easily determine the number of neutrons to be 78 (131 − 53). Not all atoms of the same element have necessarily the same number of neutrons although they all have the same number of protons. These variations (the same atomic number but different mass numbers) are called **isotopes.** As an example, the hydrogen atom has three isotopes: ${}^{1}_{1}\mathrm{H}$ (hydrogen), ${}^{2}_{1}\mathrm{H}$ (deuterium), and ${}^{3}_{1}\mathrm{H}$ (tritium).

Based on previous discussion, it is known that an amu provides us with a relative measure of the mass of an atom with respect to the carbon atom. But how do we find the mass of one atom in grams? Well, it was experimentally determined that the number of atoms in 12 grams of ${}^{12}\mathrm{C}$ is 6.02×10^{23} (called *Avogadro's number* in honor of the Italian scientist[12]). To appreciate the magnitude of this number, consider that if you could distribute 6.02×10^{23} pennies equally among the population of the earth (~6 billion) each person would receive over 1.0 trillion dollars! One **mole** or **gram-mole** (mol) of any element is then defined as the amount of substance that contains 6.02×10^{23} atoms. Avogadro's number corresponds to the number of atoms needed to create a mass in units of grams numerically equal to the atomic mass in amu of the substance under consideration. For instance, one atom of ${}^{12}\mathrm{C}$ has an atomic mass of 12 amu, while one mole of ${}^{12}\mathrm{C}$ has a mass of 12 grams and contains 6.02×10^{23} atoms; this mass is called the *relative atomic mass*, *molar mass*, or the *atomic weight*. It is important to note that the relative atomic mass of each element reported in most textbooks (including this one) represents the *average relative atomic mass* of that element for all its naturally occurring isotopes weighed by their isotopic abundance. For instance, the relative atomic mass for carbon is reported as 12.01 grams instead of 12 grams. This is due to some C isotopes such as ${}^{13}\mathrm{C}$ (1.07% abundant) being more massive than ${}^{12}\mathrm{C}$ (98.93% abundant).

EXAMPLE PROBLEM 2.1

The most abundant isotopes of iron, Fe, are:

${}^{56}\mathrm{Fe}$ (91.754%), with an atomic mass of 55.934 amu

${}^{54}\mathrm{Fe}$ (5.845%), with an atomic mass of 53.939 amu

${}^{57}\mathrm{Fe}$ (2.119%), with an atomic mass of 56.935 amu

${}^{58}\mathrm{Fe}$ (0.282%), with an atomic mass of 57.933 amu

---

[12] Amedeo Avogadro (1776–1856). Italian scientist and professor of physics at the University of Turin.

■ **Solution**

a. Find the average atomic mass of Fe.

$$\begin{aligned}&[(91.754 \times 55.934) + (5.845 \times 53.939) + (56.935 \times 2.119)\\&\quad + (0.282 \times 57.933)]/100 = 55.8 \text{ amu (mass of one Fe atom in amu)}\end{aligned}$$

b. What is the relative atomic mass of iron?
As discussed previously, the relative atomic mass will have numerically the same value as the average atomic mass but with units of grams, 55.849 grams. Compare this value to that reported in the periodic table, Fig. 2.3.

c. How many atoms are there in 55.849 grams of Fe?

$$6.02 \times 10^{23} \text{ atoms}$$

d. How many atoms are there in one gram of Fe?

$$\begin{aligned}&1 \text{ g Fe} \times (1 \text{ mol Fe}/55.849 \text{ g Fe}) \times (6.02 \times 10^{23} \text{ atoms Fe}/ 1 \text{ mol Fe})\\&= 1.078 \times 10^{22} \text{ atoms of Fe}\end{aligned}$$

e. What is the mass in grams of one atom of Fe?

$$55.849 \text{ g} / 6.02 \times 10^{23} \text{ atoms} = 9.277 \times 10^{-23} \text{ gram/atom.}$$

f. Based on the answer in part e, what is the mass in grams of one amu? The average atomic mass of Fe is found to be 55.846 amu in part a. In part e, the corresponding mass in grams is found to be 9.277×10^{-23} gram. The mass in grams of one amu is therefore $9.277 \times 10^{-23}/55.846 = 1.661 \times 10^{-24}$ g.

EXAMPLE PROBLEM 2.2

An intermetallic compound has the chemical formula Ni_xAl_y, where x and y are simple integers, and consists of 42.04 wt% nickel and 57.96 wt% aluminum. What is the simplest formula of this nickel aluminide?

■ **Solution**

We first determine the mole fraction of nickel and aluminum in this compound. Using a basis of 100 g of the compound, we have 424.04 g of Ni and 57.96 g of Al. Thus,

$$\begin{aligned}\text{No. of moles of Ni} &= 42.04 \text{ g Ni} \times (1 \text{ mol Ni} /58.71 \text{ g Ni}) = 0.7160 \text{ mol}\\\text{No. of moles of Al} &= 57.96 \text{ g Al} \times (1 \text{ mol Al} /26.98 \text{ g Al}) = 2.148 \text{ mol}\\&\qquad\qquad\qquad\qquad\qquad\qquad \text{Total} = 2.864 \text{ mol}\end{aligned}$$

Thus,

$$\begin{aligned}\text{mole fraction of Ni} &= 0.1760 / 2.864 = 0.25\\\text{mole fraction of Al} &= 2.148 / 2.864 = 0.75\end{aligned}$$

The simplest formula in terms of gram-mole fraction becomes $Ni_{0.25}Al_{0.75}$. To express this in integer form we multiply both fractions by four, resulting in $NiAl_3$.

Dmitri Mendeleev[13] first organized the elements in a table that has evolved to what we now call the *periodic table*. He ordered the elements in a horizontal row according to their relative atomic mass. He then started a new row when he found an element that had similar chemical properties to one of the elements in the previous row. After completing his table, he noticed that the elements in the same column had similar chemical characteristics. He also noticed that some columns contained empty spots that he attributed to elements not being found yet (e.g., gallium and germanium). These elements were later found and had properties close to what Mendeleev had suggested.

Later, scientists observed that arranging the elements based on increasing atomic number, Z, instead of relative atomic mass, reveals a periodic behavior. This behavior is referred to as the **law of chemical periodicity,** which states that the properties of elements are functions of their atomic number in a periodic manner. A new periodic table based on this number (z) was developed by H.G.J. Moseley. [14] An updated version of this table is presented in Fig. 2.3. Note that each horizontal row of elements is called a *period* (i.e., first period, second period, . . . seventh period), and each vertical column of the elements is called a *group* (i.e., group 1A, 2A, . . . 8A). The transition and the inner transition elements (heavy metals) are also shown. Each element is presented by its chemical symbol above which the atomic number is presented. Below the symbol, the atomic mass, in amu, or the relative molar mass, in grams, is presented (recall they are the same number). As an example, based on the information in the periodic table, aluminum has 13 protons ($Z = 13$); one mole of aluminum has a mass of 26.98 grams (or 26.98 grams/mol) and contains 6.02×10^{23} atoms. Thus far, 109 elements have been discovered and named ranging from hydrogen with an atomic number of 1 to meitnerium with an atomic number of 109 (six other are discovered but yet to be named).

2.3 THE ELECTRONIC STRUCTURE OF ATOMS

2.3.1 Planck's Quantum Theory and Electromagnetic Radiation

In the early 1900s, Max Planck,[15] a German scientist, discovered that atoms and molecules emit energy only in certain discrete quantities, called **quanta.** Prior to that, scientists believed that energy in any amount (continuous) could be emitted from an atom. Max Planck's *quantum theory* altered the direction of science. To understand his discovery, we must first understand the nature of waves.

There are many different types of waves such as water waves, sound waves, and light waves. In 1873, James Clerk Maxwell[16] proposed that the nature of visible light is in the form of electromagnetic radiation. In **electromagnetic radiation,**

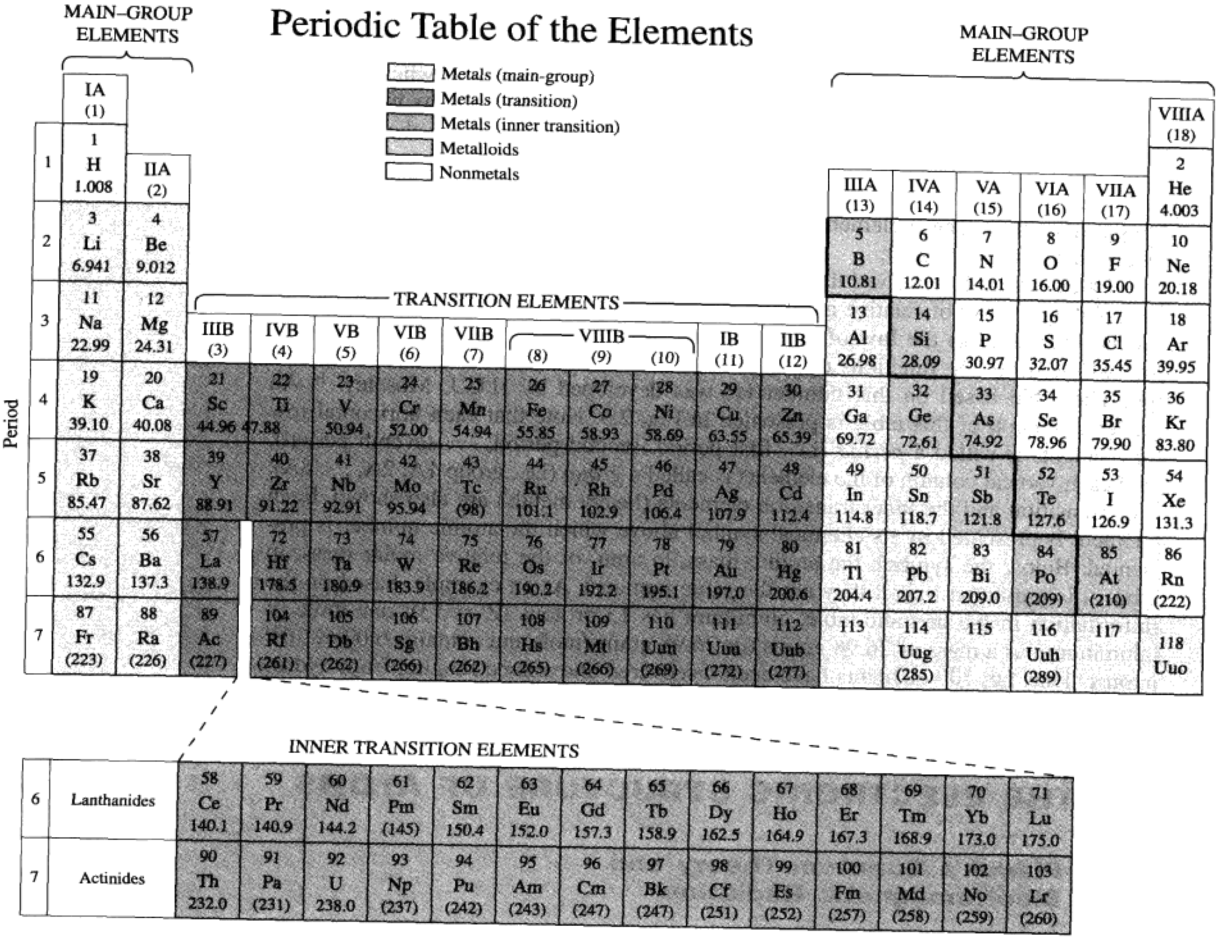
---

[13] Dmitri I. Mendeleev (1834–1907). Russian chemist and inventor.

[14] Henry G.J. Moseley (1887–1915). English physicist.

[15] Max Karl Ernst Ludwig Planck (1858–1947). German physicist and Nobel laureate (1918). Three of his doctoral students received Nobel prizes.

[16] James Clerk Maxwell (1831–1879). Scottish mathematician and physicist.



Periodic Table of the Elements

░ Metals (main-group)
▓ Metals (transition)
▒ Metals (inner transition)
▒ Metalloids
☐ Nonmetals

MAIN–GROUP ELEMENTS — TRANSITION ELEMENTS — MAIN–GROUP ELEMENTS

Period	IA (1)	IIA (2)	IIIB (3)	IVB (4)	VB (5)	VIB (6)	VIIB (7)	VIIIB (8)	VIIIB (9)	VIIIB (10)	IB (11)	IIB (12)	IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	VIIIA (18)
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	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
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	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 (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Uun (269)	111 Uuu (272)	112 Uub (277)	113	114 Uug (285)	115	116 Uuh (289)	117	118 Uuo

INNER TRANSITION ELEMENTS

6	Lanthanides	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	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
7	Actinides	90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Figure 2.3
The updated periodic table showing seven periods, eight main group elements, transition elements, and inner transition elements. Note that the majority of the elements are classified as metals or metalloids.

energy is released and transmitted in the form electromagnetic waves. Electromagnetic waves travel at a speed of light, *c*, 3.00×10^8 meters per second (186,000 miles/s) in vacuum.

Just like any other wave, the important characteristics that define the electromagnetic waves are wavelength (often given in nm or 10^{-9} m), frequency (s^{-1} or

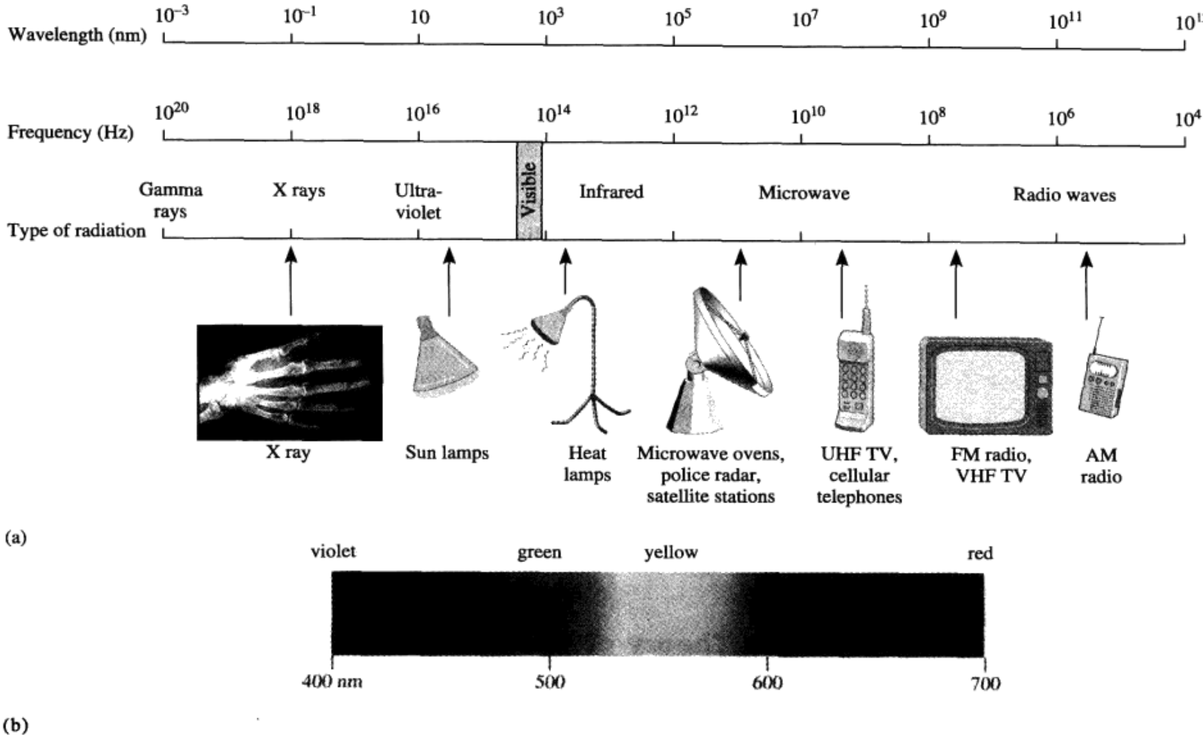

Wavelength (nm)
10^{-3}
10^{-1}
10
10^{3}
10^{5}
10^{7}
10^{9}
10^{11}
10
Frequency (Hz)
10^{20}
10^{18}
10^{16}
10^{14}
10^{12}
10^{10}
10^{8}
10^{6}
10^{4}
Type of radiation
Gamma rays
X rays
Ultra-violet
Visible
Infrared
Microwave
Radio waves
X ray
Sun lamps
Heat lamps
Microwave ovens, police radar, satellite stations
UHF TV, cellular telephones
FM radio, VHF TV
AM radio
(a)
violet
green
yellow
red
400 nm
500
600
700
(b)

Figure 2.4
Electromagnetic spectrum extending from low wavelength, high frequency, Gamma rays to large wavelength, low frequency radio waves. (*a*) The full spectrum. (*b*) Visible spectrum.
(© Getty/RF.)

Hz), and speed (m/sec). The speed of the wave, c, is related to its frequency, ν, and wave length, λ, as follows:

$$\nu = \frac{c}{\lambda} \tag{2.1}$$

A variety of electromagnetic waves including radio, microwave, infrared, visible, ultraviolet, X-ray, and gamma ray waves are presented in Fig. 2.4. These waves differ from each other according to their wavelengths and frequencies. For instance, a radio antenna produces large wavelengths (10^{12} nm ~ 1 km) and low frequencies (10^{6} Hz); a microwave oven produces microwaves with wavelengths of around 10^{7} nm (significantly shorter than radio waves) and frequencies of 10^{11} Hz (significantly higher than radio waves). As the wavelength decreases and frequency increases, we reach the infrared range of 10^{3} nm wavelength and 10^{14} Hz frequency (heat lamps operate in this range). When the wavelength is in the range of 700 nm (red light) to 400 nm (violet), the resulting radiation is visible (visible range). The ultraviolet rays (10 nm), X-rays (0.1 nm), and gamma rays (0.001 nm) are again in the invisible range.

When, for example, a tungsten filament is heated, its atoms emit energy in the form of electromagnetic radiation that appears as visible white light to us. Planck suggested that energy emitted from the atoms associated with this radiation is emitted in a quantum form. The energy of a single quantum of energy is given by the following equation where h is the Planck's constant, 6.63×10^{-34} J·s, where J is Joule, and ν is the frequency of radiation (Hz).

$$E = h\nu \tag{2.2}$$

More specifically, according to Planck, energy is always released in integer multiples of $h\nu$ ($1h\nu$, $2h\nu$, $3h\nu$, . . .) and never in noninteger multiples, for instance 1.34 $h\nu$. Equation 2 also implies that as the frequency of radiation increases, its energy will also increase. Thus, when referring to the electromagnetic spectrum, gamma rays produce higher energies than X-rays, X-rays higher than ultraviolet rays, and so on.

Inserting Eq. 2.1 into Eq. 2.2, the energy associated with a form of radiation can also be calculated in terms of the wavelength of the radiation:

$$E = \frac{hc}{\lambda} \tag{2.3}$$

2.3.2 Bohr's Theory of the Hydrogen Atom

In 1913, Neils Bohr[17] used Max Planck's quantum theory to explain how the excited hydrogen atom absorbs and emits only certain wavelengths of light, a phenomenon that had yet to be explained. He suggested that electrons travel in circular paths around the nucleus with discrete angular momenta (a product of velocity and radius). Furthermore, he suggested that the energy of the electron is restricted to a specific energy level that places the electron at that fixed circular distance from the nucleus. He called this the *orbit* of the electron. If the electron loses or gains a specific amount of energy, it will then change its orbit to another circular orbit at a fixed distance from its nucleus (Fig. 2.5). In his model, the value of the orbit, the principal quantum number n, can range from 1 to infinity. The energy of the electron and the size of its orbit increases as n increases. The $n = 1$ orbit represents the lowest energy state and is therefore closest to the nucleus. The normal state of the hydrogen electron is at $n = 1$ and is called the *ground state*. For an electron to move from a lower orbit, for instance, the ground state, $n = 1$, to a higher excited state, $n = 2$, a specific amount of energy must be absorbed (Fig. 2.5). In contrast, when the electron drops from the excited state, $n = 2$, to the ground state, $n = 1$, the same amount of energy must be released. As discussed previously, this quantum of energy emitted or released will be in the form electromagnetic radiation, called a **photon,** with a specific wavelength and frequency.

---

[17] Neils Henrik Davis Bohr (1885–1962). Danish physicist and Nobel laureate (1922).

Bohr developed a model for the determination of the allowed energy of the hydrogen electron depending on its quantum state, n (Fig. 2.6). Only energy levels according to this equation were allowed.

$$E = -2\pi^2 me^4/n^2\mathrm{h}^2 = \frac{-13.6}{n^2\ \mathrm{eV}} \tag{2.4}$$

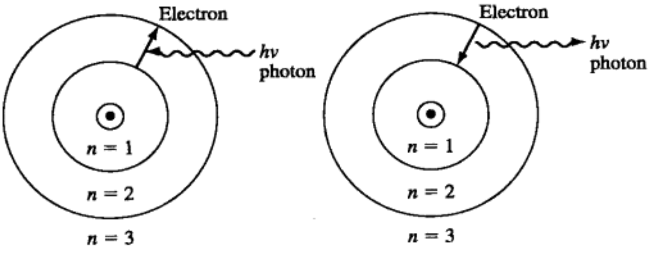
where m and e are the mass and the charge of the electron, respectively, and 1 eV $= 1.60 \times 10^{-19}$ J. The negative sign was used because Bohr assigned zero to the energy of a completely separated electron with no kinetic energy at n = infinity. Thus, the energy of any electron at a lower orbit would be negative. According to Bohr's equation, the energy of the electron in the ground state, $n = 1$, is -13.6 eV. In order to separate that electron from its nucleus, energy must be absorbed by the electron. The minimum energy required to accomplish this is called the **ionization energy.** As n increases, the energy associated with the electron in that orbit also increases (becomes less negative). For instance when $n = 2$, the corresponding energy level for the electron is $-13.6/2^2$ or -3.4 eV.

Bohr explained the quantity of energy released or absorbed by the electron as it changed orbits based on the difference in the energy of the electron between the final and initial orbits ($\Delta E > 0$ when energy is released and $\Delta E < 0$ when energy is absorbed).

$$\Delta E = E_f - \mathrm{E}_i = -13.6\ (1/n_f^{\,2} - 1/n_i^{\,2}) \tag{2.5}$$

where f and i represent the final and the initial states of the electron, respectively. For instance, the energy associated with a transition from $n = 2$ to $n = 1$, would result in a $\Delta E = E_2 - E_1 = -13.6\ (1/2^2 - 1/1^2) = 13.6 \times 0.75 = 10.2$ eV. The electron emits a photon of 10.2 eV as it drops to $n = 1$ (energy is released). The wavelength of this photon is determined according to $\lambda = hc/E = (6.63 \times 10^{-34}\ \mathrm{J{\cdot}s})\ (3.00 \times 10^8\ \mathrm{m/sec})/10.2\ \mathrm{eV}\ (1.6 \times 10^{-19}\ \mathrm{J/eV}) = 1.2 \times 10^{-7}$ m or 120 nm. From Fig. 2.4, this wavelength corresponds to the ultraviolet range.

Various possible transitions of the hydrogen electron or the emission spectrum of hydrogen are presented in Fig. 2.6. In this figure, each horizontal line represents



(a) Energy absorbed (b) Energy emitted

Figure 2.5
(a) The hydrogen electron being excited into a higher orbit. (b) An electron in a higher energy orbit dropping to a lower orbit, resulting in the emission of a photon of energy $h\nu$. (This figure is only acceptable for Bohr's model.)

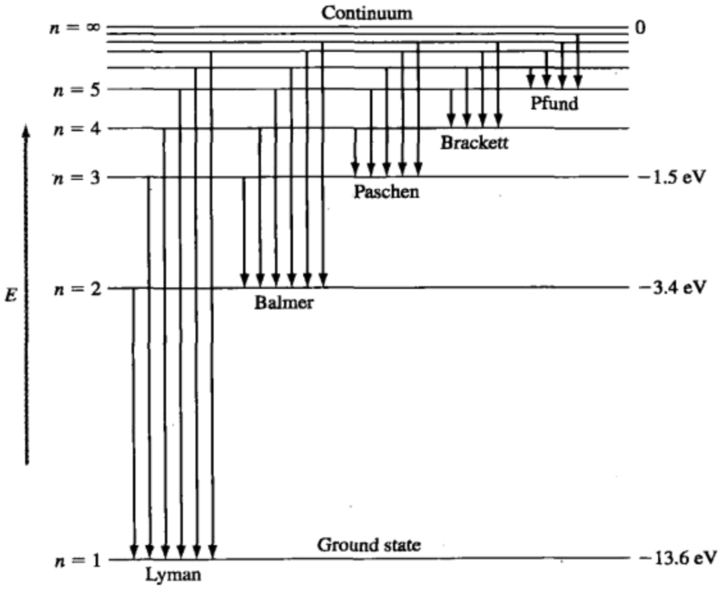


Figure 2.6
Energy-level diagram for the line spectrum of hydrogen.
(From F.M. Miller, Chemistry: Structure and Dynamics, McGraw-Hill, 1984, p. 141. Reproduced with permission of The McGraw-Hill Companies.)

an acceptable energy level or orbit, according to principal quantum number *n*, for the hydrogen electron. The visible emissions, all fall under the Balmer series. The Lyman series corresponds to the ultraviolet emissions while the Paschen and the Brackett series correspond to infrared emissions.

EXAMPLE PROBLEM 2.3

A hydrogen atom exists with its electron in the $n = 3$ state. The electron undergoes a transition to $n = 2$ state. Calculate (a) the energy of the corresponding photon, (b) its frequency, and (c) its wavelength. (d) Is the energy absorbed or emitted, and (e) which series does it belong to and what specific type of emission does it represent?

■ Solution

a. Energy of the photon emitted is

$$E = \frac{-13.6\text{ eV}}{n^2} \tag{2.3}$$

$$\Delta E = E_3 - E_2$$

$$= \frac{-13.6}{3^2} - \frac{-13.6}{2^2} = 1.89\text{ eV} \blacktriangleleft$$

$$= 1.89\text{ eV} \times \frac{1.60 \times 10^{-19}\text{ J}}{\text{eV}} = 3.02 \times 10^{-19}\text{ J} \blacktriangleleft$$

b. The frequency of the photon is

$$\Delta E = h\nu$$

$$\nu = \frac{\Delta E}{h} = \frac{3.02 \times 10^{-19}\,\mathrm{J}}{6.63 \times 10^{-34}\,\mathrm{J \cdot s}}$$

$$= 4.55 \times 10^{14}\,\mathrm{s^{-1}} = 4.55 \times 10^{14}\,\mathrm{Hz} \blacktriangleleft$$

c. The wavelength of the photon is

$$\Delta E = \frac{hc}{\lambda}$$

or

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34}\,\mathrm{J \cdot s})(3.00 \times 10^{8}\,\mathrm{m/s})}{3.02 \times 10^{-19}\,\mathrm{J}}$$

$$= 6.59 \times 10^{-7}\,\mathrm{m}$$

$$= 6.59 \times 10^{-7}\,\mathrm{m} \times \frac{1\,\mathrm{nm}}{10^{-9}\,\mathrm{m}} = 659\,\mathrm{nm} \blacktriangleleft$$

d. Energy is released as its quantity is positive, and the electron is transitioning from a higher orbit to a lower orbit.

e. The emission belongs to the Blamer series (Fig. 2.6) and corresponds to the visible red light (Fig. 2.4).

2.3.3 The Uncertainty Principle and Schrodinger's Wave Functions

Although Bohr's model worked very well for a simple atom such as hydrogen, it did not explain the behavior of more complex (multielectron) atoms and left many unanswered questions. Two new discoveries helped scientists explain the true behavior of the atom. The first was the proposal by Louis de Broglie[18] that particles of matter such as electrons could be treated in terms of both particle and wave (similar to light). He proposed that the wavelength of an electron (or any other particle) can be determined by determining the product of its mass and its speed (its momentum) using Eq. 2.6.

$$\lambda = \frac{h}{mv} \tag{2.6}$$

Later, Werner Heisenberg[19] proposed the **uncertainty principle** stating that it is impossible to simultaneously determine the exact position and the exact momentum of a body, for instance an electron. The uncertainty principle is mathematically expressed by Eq. 2.7 where h is the Planck's constant, Δx is the uncertainty in the position, and Δu is the uncertainty in speed.

$$\Delta x \cdot m\Delta u \geq \frac{h}{4\pi} \tag{2.7}$$

---

[18] Louis Victor Pierre Raymond de Broglie (1892–1987). French physicist and Nobel laureate (1929).

[19] Werner Karl Heisenberg (1901–1976). German physicist and Nobel laureate (1932).

EXAMPLE PROBLEM 2.4

If, according to de Broglie, all particles could be viewed in terms of both wave and particles properties, then compare the wavelength of an electron moving at 16.67 percent of the speed of light with that of a baseball with a mass of 0.142 kg traveling at 96.00 mi/hr (42.91 m/s). What is your conclusion?

■ Solution

According to Eq. 2.6, we need the mass and speed of the particle to determine the particle's wavelength. Accordingly,

$$\lambda_{\text{electron}} = \frac{h}{mv} = \frac{6.62 \times 10^{-34}\ \text{kg} \cdot \text{m}^2/\text{s}}{(9.11 \times 10^{-31}\ \text{kg})(0.1667 \times 3.0 \times 10^8\ \text{m/s})}$$

$$= 1.5 \times 10^{-10}\ \text{m} = 0.15\ \text{nm}$$

(note the diameter of the atom is about 0.1 nm)

$$\lambda_{\text{baseball}} = \frac{6.62 \times 10^{-34}\ \text{kg} \cdot \text{m}^2/\text{s}}{(0.142\ \text{kg})\,(42.91\ \text{m/s})} = 1.08 \times 10^{-34}\ \text{m}$$

$$= 1.08 \times 10^{-25}\ \text{nm}$$

The wavelength of a baseball 10^{24} times smaller (much too short to observe) than that of an electron. In general, particles with ordinary size will have immeasurably small wavelengths and we can not determine their wave properties.

EXAMPLE PROBLEM 2.5

For the above problem, if the uncertainty associated with the measurement of the speed of the baseball is (a) 1 percent, and (b) 2 percent, what are the corresponding uncertainties in knowing the position of the baseball? What is your conclusion?

■ Solution

According to Eq. 2.7, we will first calculate the uncertainty in the measurement of the speed to be (0.01 × 42.91 m/s) = 0.43 for part (a) and (0.02 × 42.91) = 0.86 m/s for part (b).

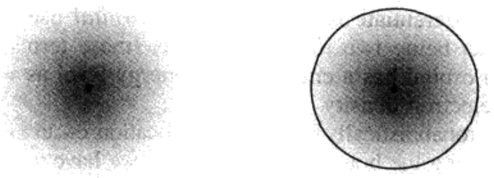
a. Rewriting Eq. 2.7 gives:

$$\Delta x \geq \frac{h}{4\pi m \Delta u} \geq \frac{6.62 \times 10^{-34}\,\text{kg} \cdot \text{m}^2/\text{s}}{4\pi(0.142\ \text{kg})(0.43\ \text{m/s})} \geq 8.62 \times 10^{-34}\,\text{m}$$

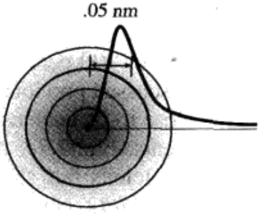
b. Rewriting Eq. 2.7 gives:

$$\Delta x \geq \frac{h}{4\pi m \Delta u} \geq \frac{6.62 \times 10^{-34}\,\text{kg} \cdot \text{m}^2/\text{s}}{4\pi(0.142\ \text{kg})(0.86)} \geq 4.31 \times 10^{-34}\,\text{m}$$

As the uncertainty with measurement of speed increases, the uncertainty in measurement of position decreases.



(*a*) electron density plot (*b*) bountry surface



(*c*) radial probability

Figure 2.7
(*a*) The electron density plot for the hydrogen electron in the grounded state, (*b*) the 90-percent boundary surface diagram, and (*c*) successive spherical shells and radial probability distribution (dark line).

Heisenberg's reasoning was that any attempt at measurement would alter the velocity and position of the electron. Heisenberg also rejected Bohr's concept of an "orbit" of fixed radius for an electron; he asserted that the best we can do is to provide the probability of finding an electron with a given energy within a given space.

The understanding was nearly completed when Erwin Schrodinger[20] used the *wave equation* to explain the behavior of electrons. Solution of the wave equation is in terms of a wave function, ψ (psi). The square of the wave function, ψ^2, presents the probability of finding an electron of a given energy level in a given region of space. The probability is called **electron density** and can be graphically expressed by an array of dots (called the *electron cloud*), each dot expressing a possible position of the electron with a specific energy level. For instance, the electron density distribution in Fig. 2.7*a* is for the ground state hydrogen atom. Although the general shape is spherical (as Bohr suggested), it is clear according to this model that the electron can exist at any given position relative to the nucleus. Also, the highest probability of finding an electron, in the ground state, is very close to the nucleus (where the density of dots is the highest). Moving away from the nucleus, the probability of finding an electron decreases.

---

[20] Erwin Rudolf Josef Alexander Schrodinger (1887–1961). Austrian physicist and Nobel laureate (1933).

If one solves the wave equation, different wave functions and thus electron density graphs will be generated. These wave functions are called the **orbitals.** We would like to immediately differentiate between the term *orbital* used here and the term *orbit* used by Bohr as being two distinct concepts (these terms must not be used interchangeably). An orbital has a characteristic energy level as well as a characteristic distribution of electron density.

Another way to probabilistically represent the location of an electron with a given energy level is by drawing the boundary inside which we have a 90-percent chance of finding that electron. For the ground state electron, there is a 90-percent probability of finding an electron within a sphere of radius 100 pm. The sphere in Fig. 2.7*b* is an alternative to the electron density diagram and is called the **boundary surface** representation. Note that a boundary surface of 100-percent probability for the same electron would have infinite dimensions. As discussed previously, the highest probability of finding an electron in Fig. 2.7*a* is very close to its nucleus; however, if we divide the sphere into equally spaced concentric segments, Fig. 2.7*c*, the *total probability* of finding an electron will be highest not at the nucleus but slightly farther away from it. Total probability, also called the *radial probability*, considers the probability of the electron being at a spherical layer with respect to the volume of that layer. Near the nucleus, for instance in the first layer, the probability is high but the volume is small; in the second layer, the probability of finding an electron is less than the first layer but the volume of the second layer is much larger (increase in volume is more than decrease in probability) and thus the total probability of observing an electron is higher in the second layer. This second layer is located near the nucleus at a distance of 0.05 nm or 50 pm as shown in Fig. 2.7*c*. This effect diminishes as the distance from the nucleus increases because the probability levels drop much faster than the volume of the layer increases.

Boundary surface diagrams for electrons of higher energy levels become more complicated and are not necessarily spherical. This will be discussed in more detail in the future sections.

2.3.4 Quantum Numbers, Energy Levels, and Atomic Orbitals

The modern quantum mechanics proposed by Schrodinger and others requires a set of four integers called the *quantum numbers* to identify the energy and the shape of the boundary space, or the electron cloud, and the spin for any electron in any atom. We are no longer limited to the hydrogen atom. The first quantum numbers are n, ℓ, m_ℓ, and m_s.

The Principal Quantum Number, n: Principal Energy Levels or Shells The **principal quantum number, n,** is the most important in determining the energy level of the electron under consideration. It only takes on integer values of one or greater than one, i.e., $n = 1, 2, 3, \ldots$. Each principal energy level is also known as a *shell* representing a collection of subshells and orbitals with the same principal number, n. As n increases, so does the energy of the electron under consideration, indicating that the electron is less tightly bonded to the nucleus (easier to ionize). Finally, as n increases, the probability of finding the electron farther from the nucleus also increases.

The Subsidiary or Orbital Quantum Number, ℓ: Subshells Within each principal shell, *n*, there exist subshells. When $n = 1$, there is only one kind of subshell possible, one similar to that presented in Fig. 2.7. When $n = 2$, however, two different subshells are possible, and three different subshells when $n = 3$, and so on. The subshells are represented by the **orbital quantum number,** ℓ. The shape of the electron cloud or the boundary space of the orbital is determined by this number. The quantum number ℓ may be represented by an integer ranging from 0 to $n - 1$, or by letters.

Number designation $\ell = 0, 1, 2, 3, .., n - 1$

Letter designation $\ell = s, p, d, f, \ldots$

Thus for $n = 1$, $\ell = s$; for $n = 2$, $\ell = s$ or p; for $n = 3$, $\ell = s$, p, or d; and so on. Therefore, the representation 3s represents a principal energy level, *n*, of 3 and the subshell, ℓ, of s.

The s subshell ($\ell = 0$), regardless of n, always looks spherical (Fig. 2.8*a*). However, as *n* becomes larger, the size of the sphere increases, indicating that the electrons can travel farther from the nucleus.

The p subshells ($\ell = 1$) are not spherical. In fact they are dumbbell shaped with two electron density lobes on either side of the nucleus (Fig. 2.8*a*). There are three p orbitals within a given subshell, and they are different in their orientation in space. The three orbitals are mutually perpendicular. The d subshells are significantly more complicated in shape, Fig. 2.8*c*, and play an important role in the chemistry of transition metal ions.

The Magnetic Quantum Number, $m\ell$: Orbitals and Their Orientations The **magnetic quantum number,** m_ℓ, represents the orientation of the orbitals within each subshell. The quantum number m_ℓ, will take on values ranging from $+\ell$ to $-\ell$. For instance when $\ell = 0$ or s, the corresponding m_ℓ is 0; when $\ell = 1$ or p, the corresponding m_ℓ is -1, 0, and $+1$; when $\ell = 2$ or d, the corresponding m_ℓ is -2, -1, 0, $+1$, $+2$, and so on. Thus, for every subshell, ℓ, there are $2\,\ell + 1$ orbitals within the subshell. In terms of s, p, d, and f, there is a maximum of one s, three p, five d, and seven f orbitals in each subenergy level. The total number of orbitals in a principal shell (including all available subshells) can be expressed as n^2; for instance, one orbital in $n = 1$, four orbitals in $n = 2$, and nine orbitals in $n = 3$. Orbitals with the same subshell have the same energy level. The boundary space diagrams of s, p, and d orbitals are shown in Fig. 2.8. It is important to note that the size of boundary spaces becomes larger as *n* increases, indicating the higher probability of finding an electron with that energy level farther from the nucleus of the atom.

The Spin Quantum Number, m_s: Electron Spin In the helium atom ($Z = 2$), both electrons are occupying the first principal shell ($n = 1$), the same subshell ($\ell = 0$ or s), and the same magnetic quantum number ($m_\ell = 0$). Do these two electrons have identical quantum numbers? To completely describe any electron in an atom, in addition to *n*, ℓ, and m_ℓ, we must also identify its **spin quantum number,** m_s. The spin quantum number can take on either $+\frac{1}{2}$ or $-\frac{1}{2}$. The electron can have

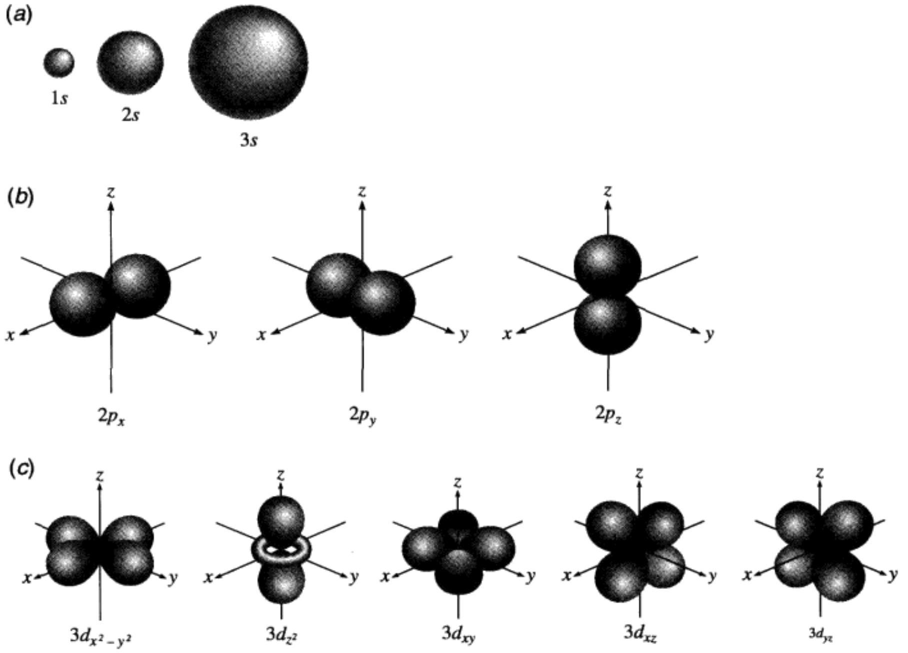


Figure 2.8.
Schematic diagram of (*a*) s, (*b*) p, and (*c*) d orbitals.

only the two directions of spin and no other position is allowed. In addition, according to **Pauli's exclusion principle,** no more than two electrons can occupy the same orbital of an atom, and the two electrons must have opposite spins. In other words, no two electrons can have the same set of four quantum numbers. For instance, in the atom of He, what makes its two electrons distinct from a quantum mechanics point of view is the spin quantum number; $m_s = \frac{1}{2}$ for one and $m_s = -\frac{1}{2}$ for the other. A summary of the allowed values of the quantum numbers is presented in Table 2.2.

Since only two electrons can occupy a single orbital and since each principal energy level or shell, n, allows n^2 orbitals, a general rule may be stated that each principal energy level can accommodate a maximum number of $2n^2$ electrons

Table 2.2 Allowed values for the quantum numbers of electrons

n	Principal quantum number	n 5 1, 2, 3, 4, . . .	All positive integers
ℓ	Subsidiary quantum number	$\ell = 0, 1, 2, 3, \ldots, n + 1$	n allowed values of ℓ
m_ℓ	Magnetic quantum number	Integral values from $-\ell$ to $+\ell$ including zero	$2\ell + 1$
m_s	Spin quantum number	$+\frac{1}{2}, -\frac{1}{2}$	2

Table 2.3 Maximum number of electrons for each principal atomic shell

Shell number, n (principal quantum number)	Maximum number of electrons in each shell ($2n^2$)	Maximum number of electrons in orbitals
1	$2(1^2) = 2$	s^2
2	$2(2^2) = 8$	s^2p^6
3	$2(3^2) = 18$	$s^2p^6d^{10}$
4	$2(4^2) = 32$	$s^2p^6d^{10}f^{14}$
5	$2(5^2) = 50$	$s^2p^6d^{10}f^{14}\ldots$
6	$2(6^2) = 72$	$s^2p^6\ldots$
7	$2(7^2) = 98$	$s^2\ldots$

(Table 2.3). For instance, the $n = 2$ principal energy level can accommodate a maximum of $2(2)^2 = 8$ electrons; two in its s subshell and six in its p subshell, which itself contains three orbitals.

2.3.5 The Energy State of Multielectron Atoms

Thus far, the majority of the discussion has focused on the single electron atom of hydrogen. The single electron in this atom can be energized to various principal energy levels and regardless of the subsidiary quantum number (subshell), its energy level will be that of the principal shell in which it exists. However, when more than one electron exists, electrostatic attraction effects between the electron and the nucleus as well as repulsion effects between the electrons will lead to more complex energy states or splitting of energy levels. Thus, the energy of an orbital in a multielectron atom depends not only on its n value (size) but also on its ℓ value (shape).

For instance, consider the single electron in an H atom and the single electron in the ionized He atom (He^+). Both electrons are in the 1s orbital. However, recall that the nucleus of the He atom has two protons versus the one proton in the H nucleus. The orbital energies are -1311 kJ/mol for the H electron and -5250 kJ/mol for He^+ electron. It is more difficult to remove the He^+ electron because it has a stronger attraction to its nucleus of two protons. In other words, the higher the charge of the nucleus, the higher is the attraction force on an electron and the lower the energy of the electron (a more stable system); this is called the **nucleus charge effect.**

Let us now compare the He atom to the He^+ ion. Both have the same nucleus charge but differ in the number of electrons. The orbital energy of the 1s He electron is -2372 kJ/mol while that of He^+ is -5250 kJ/mol. It is significantly less difficult to remove one of the two electrons in the He atom than it is to remove the single He^+ electron. This is mainly due to the fact that the two electrons in the He atom repel each other and this counteracts the attraction force of the nucleus. It is almost as if the electrons shield each other from the full force of the nucleus; this is called the **shielding effect.**

Next, let us compare the Li atom ($Z = 3$) in its ground state and the first excited state of Li^{2+} ion. Note that both have a nucleus charge of $+3$, Li has two 1s electrons and one 2s electron, while Li^{2+} has one electron that is excited to its 2s level (first excited state). The orbital energy of the 2s Li electron is -520 kJ/mol while that of Li^{2+} is -2954 kJ/mol. It is easier to remove the 2s electron in the Li atom because the pair of 1s electrons in the inner shell shield the 2s electron from the nucleus (a majority of the time). The 2s electron in the Li^{2+} does not have the 1s pair and is therefore attracted strongly to its nucleus. Thus, the inner electrons shield the outer electrons and do so more effectively than electrons in the same sublevel (compare the orbital energy levels with those in the previous paragraph).

Finally, we will compare the Li atom in its ground state with the Li atom excited to its first level. The ground state Li atom has its outer electron in the 2s orbital while the excited Li atom has its outer electron in the 2p orbital. The orbital energy of the 2s electron is -520 kJ/mol while that of the 2p electron is -341 kJ/mol. Thus, the 2p orbital has a higher state of energy than the 2s orbital. This is because the 2s electron spends part of its time penetrating closer to the nucleus (much more than the 2p electron), thus having stronger attraction to the nucleus, less energy, and a more stable state. We can further generalize that for multielectron atoms, in a given principal shell, n, the lower the value of ℓ, the lower will be the energy of the subshell. (i.e., $s < p < d < f$.)

The above exercise shows that due to various electrostatic effects, the principal energy levels, n, split into several subenergy levels, ℓ, as shown in Fig. 2.9. This figure shows the order in which the various principal and subenergy levels exist relative to each other. For instance, the electrons within 3p subshells have a higher energy than 3s and a lower energy than 3d. Note in this figure that the 4s subshell has a higher energy than the 3d subshell.

2.3.6 The Quantum-Mechanical Model and the Periodic Table

In the periodic table, the elements are classified according to their ground state electron configuration. As a result, atoms of a particular element (say Li with three electrons) contain one more electron than the element preceding it (He with two electrons). These electrons are found in principal energy shells, subshells, and orbitals. But how do we know the particular order in which the electrons fill the orbitals? The electrons fill the first available principal energy levels first. The maximum number of electrons in each principal energy level is given in Table 2.3. Next, within each principal energy level, they fill the lowest energy subshells first, i.e., s, followed by p, d, and finally f. The s, p, d, and f subenergy levels will allow a maximum of 2, 6, 10, and 14 electrons, respectively. Each subshell level will have its own energy level, and the order in which each subenergy level is filled is given by Fig. 2.9.

There are two different forms of expressing the *orbital occupancy*: (1) electron configuration and (2) orbital box diagram.

The electron configuration notation consists of the value of the principal shell, n, followed with the letter designation of the subshell, ℓ, and finally the number of electrons in that sublevel presented as a superscript. For instance, the electron configuration of oxygen, O, with eight electrons is $1s^2 2s^2 2p^4$. For oxygen, after filling the 1s orbital with two electrons, six electrons remain. According to Fig. 2.9, two of the six electrons fill the 2s orbital ($2s^2$) and the remaining four will occupy the p orbital ($2p^4$). The next element, fluoride, F, will have one more electron with a configuration of

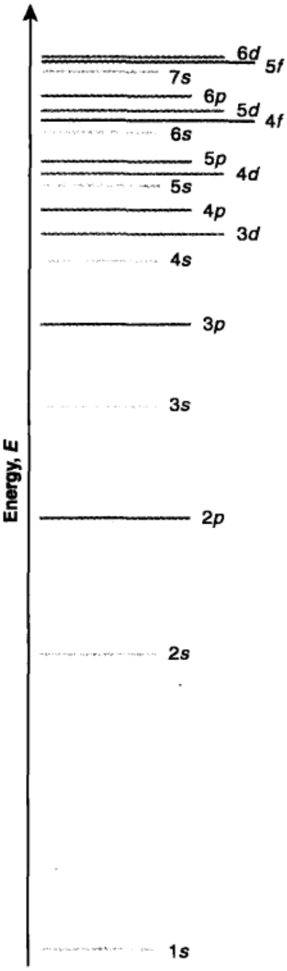


Figure 2.9
The energy level for all subenergy levels up to $n = 7$. The orbitals will fill in the same exact order.

$1s^22s^22p^5$ while the element immediately before, nitrogen, N, will have one less electron with a configuration of $1s^22s^22p^3$. To understand this more clearly, the electronic structure of the first 10 elements in the periodic table are given in Table 2.4.

Let us now consider the element scandium (Sc) with 21 electrons. The first five energy levels in increasing order of energy are (Fig. 2.9) $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$. This will account for 18 electrons. Three electrons remain to complete the electronic structure of Sc. Chronologically, one would assume that the next three electrons would

Table 2.4 Allowed values for the quantum numbers and electrons

Election Configuration		Orbital Box Diagram				
		1s	2s	2p		
H	$1s^1$	↑				
He	$1s^2$	↑↓				
Li	$1s^22s$	↑↓	↑			
Be	$1s^22s^1$	↑↓	↑↓			
B	$1s^22s^22p^1$	↑↓	↑↓	↑		
C	$1s^22s^22p^2$	↑↓	↑↓	↑	↑	
N	$1s^22s^22p^3$	↑↓	↑↓	↑	↑	↑
O	$1s^22s^22p^4$	↑↓	↑↓	↑↓	↑	↑
F	$1s^22s^22p^5$	↑↓	↑↓	↑↓	↑↓	↑
Ne	$1s^22s^22p^6$	↑↓	↑↓	↑↓	↑↓	↑↓

fill the 3d orbital, thus completing the configuration with $3d^3$. However, according to Fig. 2.9, the next orbital to be filled is 4s and not 3d. This is because the 4s energy level is lower than 3d (due to shielding and penetration effects), and as we discussed previously, the lowest energy levels are always occupied first. Therefore, the next two electrons (nineteenth and twentieth) will fill the 4s orbitals and the last electron (twenty-first) will then occupy the 3d orbital. The final configuration for Sc, in the order that the orbitals were filled, is $1s^22s^22p^63s^23p^64s^23d^1$; however, it is also acceptable to show the configuration according to the principal energy level, $1s^22s^22p^63s^23p^63d^14s^2$. Note that the inner core electrons, $1s^22s^22p^63s^23p^6$, represent the electronic structure of the noble gas argon. Thus, one can represent the electronic configuration for Sc as $[Ar]4s^23d^1$.

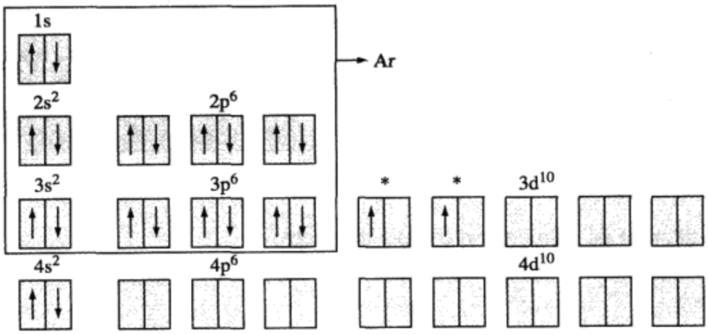
One can also show the orbital occupancy using the orbital box diagram. The advantage of the orbital box diagram is that unlike the electron configuration notation, it also shows the paired spins (opposite spin) of electrons in an orbital. The orbital box diagrams for the first 10 elements in the periodic table are presented in Table 2.4. For oxygen, O, with seven electrons, the first two electrons will occupy the 1s orbital (the lowest energy orbital) with paired spins, followed by the next two electrons occupying the 2s orbital (the next lowest energy orbital) with paired spins. The next three electrons, however, will fill the three p orbitals randomly (all p orbitals have the same energy level) with the same spin. Although the p orbital selection process is random, for convenience, we show filling up from left to right. The last electron then pairs the spin of one of the three electrons in the p orbital randomly (note the spin direction of the last electron is opposite to the other three in the p orbital). In other words, the electrons will not occupy the three p orbitals pair by pair. For element F, with one more electron than O, the next p orbital will be paired, and finally for Ne, with two more electrons than O, all three p orbitals are paired. This is also the case with the five d orbitals in the third principal shell: after each of the five d orbitals is filled with one electron of the same spin, any remaining electrons will pair the d orbitals one by one and with opposite spin.

EXAMPLE PROBLEM 2.6

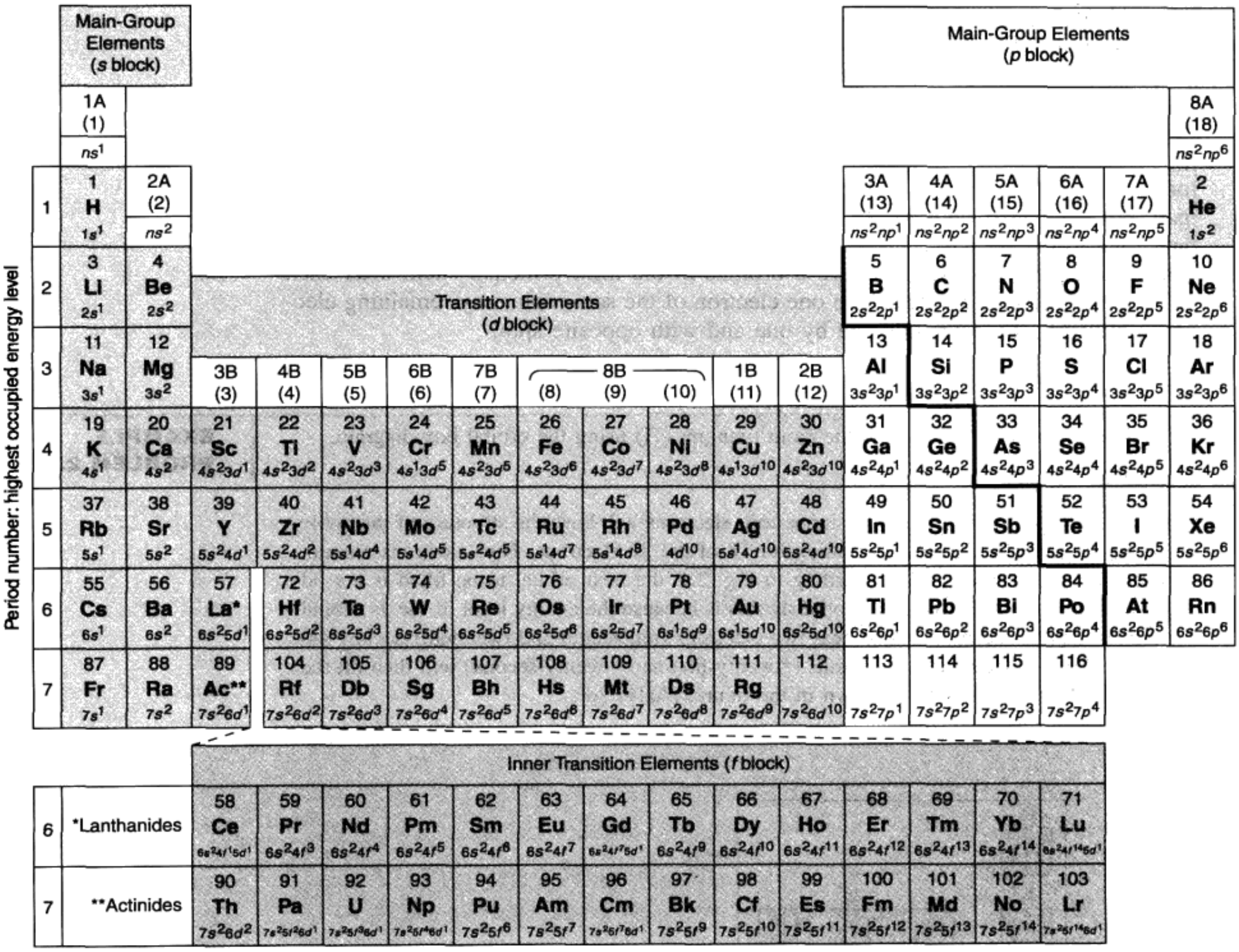
Show the electronic structure of the atom titanium (Ti) using the orbital box diagram.

■ Solution

Ti has 22 electrons. Therefore, the inner core electrons will have the structure of the noble gas argon, $\mathbf{1s^22s^22p^63s^23p^6}$, accounting for 18 of the 22 electrons. Four electrons remain. After the 3p orbital is filled, according to Fig. 2.9, the next orbital to be filled is not 3d and is instead 4s. As explained previously this is because the energy level of the 4s orbital is lower than the 3d orbital. The next two electrons (nineteenth and twentieth) occupy $4s^1$ and $4s^2$. Finally, the last two electrons (*twenty-first and *twenty-second) will then fill the available slots in d orbital as shown in the figure, $[Ar]4s^23d^2$.



It is important to note that some irregularities exist in orbital occupancy of elements and not all elements follow exactly the stated rules. For instance, one would expect that copper with 29 electrons (8 more than Sc), has an electronic structure of $[Ar]3d^94s^2$; however, it has the $[Ar]3d^{10}4s^1$ electronic structure. The reasons for these


Main-Group Elements (*s* block)
Transition Elements (*d* block)
Main-Group Elements (*p* block)
Inner Transition Elements (*f* block)
Period number: highest occupied energy level

Period	1A (1) ns^1	2A (2) ns^2	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8)	8B (9)	8B (10)	1B (11)	2B (12)	3A (13) ns^2np^1	4A (14) ns^2np^2	5A (15) ns^2np^3	6A (16) ns^2np^4	7A (17) ns^2np^5	8A (18) ns^2np^6
1	1 **H** $1s^1$																	2 **He** $1s^2$
2	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
3	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
4	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $4s^23d^1$	22 **Ti** $4s^23d^2$	23 **V** $4s^23d^3$	24 **Cr** $4s^13d^5$	25 **Mn** $4s^23d^5$	26 **Fe** $4s^23d^6$	27 **Co** $4s^23d^7$	28 **Ni** $4s^23d^8$	29 **Cu** $4s^13d^{10}$	30 **Zn** $4s^23d^{10}$	31 **Ga** $4s^24p^1$	32 **Ge** $4s^24p^2$	33 **As** $4s^24p^3$	34 **Se** $4s^24p^4$	35 **Br** $4s^24p^5$	36 **Kr** $4s^24p^6$
5	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $5s^24d^1$	40 **Zr** $5s^24d^2$	41 **Nb** $5s^14d^4$	42 **Mo** $5s^14d^5$	43 **Tc** $5s^24d^5$	44 **Ru** $5s^14d^7$	45 **Rh** $5s^14d^8$	46 **Pd** $4d^{10}$	47 **Ag** $5s^14d^{10}$	48 **Cd** $5s^24d^{10}$	49 **In** $5s^25p^1$	50 **Sn** $5s^25p^2$	51 **Sb** $5s^25p^3$	52 **Te** $5s^25p^4$	53 **I** $5s^25p^5$	54 **Xe** $5s^25p^6$
6	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La*** $6s^25d^1$	72 **Hf** $6s^25d^2$	73 **Ta** $6s^25d^3$	74 **W** $6s^25d^4$	75 **Re** $6s^25d^5$	76 **Os** $6s^25d^6$	77 **Ir** $6s^25d^7$	78 **Pt** $6s^15d^9$	79 **Au** $6s^15d^{10}$	80 **Hg** $6s^25d^{10}$	81 **Tl** $6s^26p^1$	82 **Pb** $6s^26p^2$	83 **Bi** $6s^26p^3$	84 **Po** $6s^26p^4$	85 **At** $6s^26p^5$	86 **Rn** $6s^26p^6$
7	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac**** $7s^26d^1$	104 **Rf** $7s^26d^2$	105 **Db** $7s^26d^3$	106 **Sg** $7s^26d^4$	107 **Bh** $7s^26d^5$	108 **Hs** $7s^26d^6$	109 **Mt** $7s^26d^7$	110 **Ds** $7s^26d^8$	111 **Rg** $7s^26d^9$	112 $7s^26d^{10}$	113 $7s^27p^1$	114 $7s^27p^2$	115 $7s^27p^3$	116 $7s^27p^4$		

Period	Inner Transition Elements (*f* block)														
6	*Lanthanides	58 **Ce** $6s^24f^15d^1$	59 **Pr** $6s^24f^3$	60 **Nd** $6s^24f^4$	61 **Pm** $6s^24f^5$	62 **Sm** $6s^24f^6$	63 **Eu** $6s^24f^7$	64 **Gd** $6s^24f^75d^1$	65 **Tb** $6s^24f^9$	66 **Dy** $6s^24f^{10}$	67 **Ho** $6s^24f^{11}$	68 **Er** $6s^24f^{12}$	69 **Tm** $6s^24f^{13}$	70 **Yb** $6s^24f^{14}$	71 **Lu** $6s^24f^{14}5d^1$
7	**Actinides	90 **Th** $7s^26d^2$	91 **Pa** $7s^25f^26d^1$	92 **U** $7s^25f^36d^1$	93 **Np** $7s^25f^46d^1$	94 **Pu** $7s^25f^6$	95 **Am** $7s^25f^7$	96 **Cm** $7s^25f^76d^1$	97 **Bk** $7s^25f^9$	98 **Cf** $7s^25f^{10}$	99 **Es** $7s^25f^{11}$	100 **Fm** $7s^25f^{12}$	101 **Md** $7s^25f^{13}$	102 **No** $7s^25f^{14}$	103 **Lr** $7s^25f^{14}6d^1$

Figure 2.10
The partial ground-state configuration of all elements in the periodic table.

irregularities are not completely known but one explanation is that the energy level of the corresponding 3d and 4s orbitals are extremely close for copper. Chromium, Cr, is another element that does not follow the stated rules with an electronic structure of $[Ar]3d^54s^1$. The partial ground-state configuration of all elements in the periodic table is given in Fig. 2.10 in which some of the irregularities may be observed.

2.4. PERIODIC VARIATIONS IN ATOMIC SIZE, IONIZATION ENERGY, AND ELECTRON AFFINITY

2.4.1 Trends in Atomic Size

In the previous sections, we learned that some electrons can occasionally lie far from the nucleus and this makes establishing an absolute shape for the atom difficult. To remedy this, we represented an atom as a sphere with a definite radius in which the electrons spend 90 percent of their times. In practice, however, the atomic size is determined as half the distance between the nuclei of two adjacent atoms in a solid sample of an element. This distance is also called the **metallic radius,** and we use this definition for the metallic elements in the periodic table. For other elements that commonly form covalent molecules (such as Cl, O, N, etc.), we define the atomic size as half the distance between the nuclei of the identical atoms within the molecule, called **covalent radius.** Thus, the size of an atom will depend on its immediate neighbors and varies slightly from substance to substance.

Atomic size is directly influenced by electron configuration; it therefore varies with both a period and a group. In general there are two opposing forces at work: as the principal quantum number, n, increases (moving from one period to the next in table), the electrons occupy positions farther from the nucleus and the atoms become larger. Thus, as one moves from top to bottom in a group, the size of the atom, generally, increases. On the other hand as the charge of the nucleus increases, as we move across a period (more protons), electrons are attracted more strongly to the nuclei and this tends to shrink the size of the atom. The size of an atom is therefore governed by the net effect of the two forces. This is important because atomic size influences other atomic and material properties. The general trends hold rather well for the main group elements, 1A through 8A, with some exceptions but the trends are less predictable for transition elements (Fig. 2.11).

2.4.2 Trends in Ionization Energy

The energy required to remove an electron from its atom is called the *ionization energy* (IE). The ionization energy is always positive because to remove an electron from an atom, energy must be supplied to the system. Atoms with many electrons can lose more than one electron; however, it is the energy required for the removal of the outermost electron, the **first ionization energy** (IE1) that plays the key role in the chemical reactivity of the specific atom.

Trends in first ionization energy of atoms show approximately an inverse relationship to atomic size (Fig. 2.12). In comparing Figs. 2.11 and 2.12, unlike atomic size, as we move to the right across a period, the ionization energy increases and as we move down in a group, the ionization energy drops. In other words, as the atomic size decreases, it takes more energy to remove an electron from its atom. The decrease in atomic size across a period increases the attraction between the nucleus and its electrons; thus, it is harder to remove those electrons, and the ionization

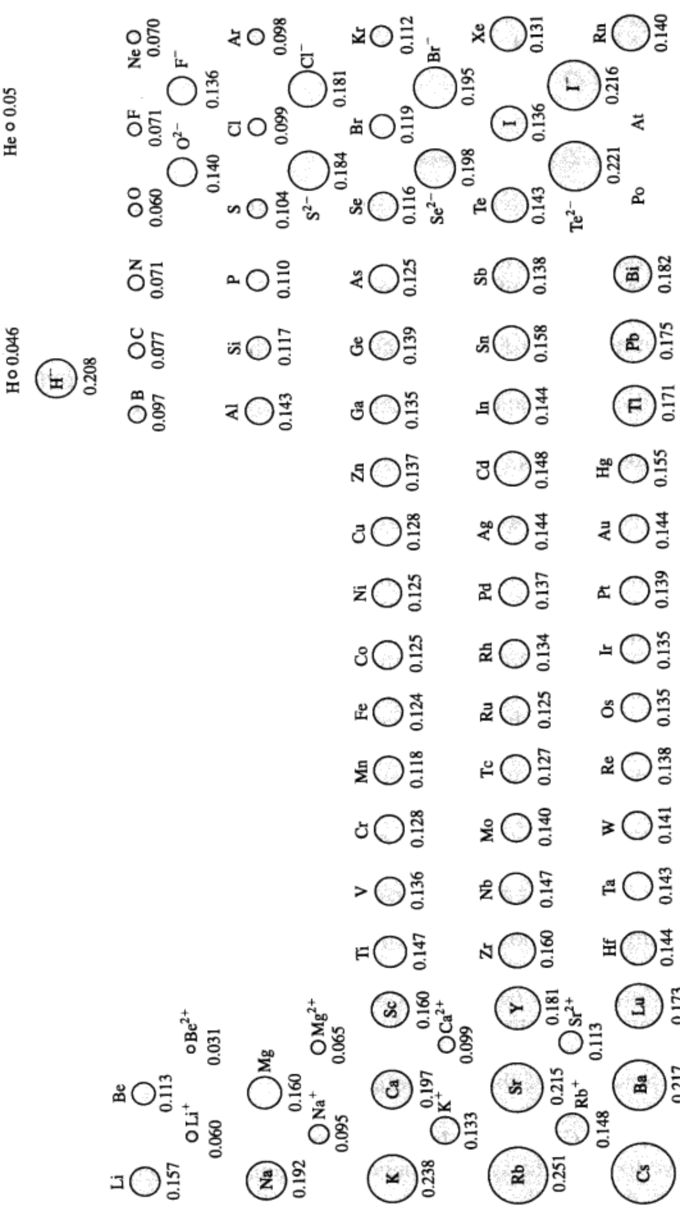

H 0.046
H^- 0.208
He 0.05
Li 0.157
Li^+ 0.060
Be 0.113
Be^{2+} 0.031
B 0.097
C 0.077
N 0.071
O 0.060
O^{2-} 0.140
F 0.071
F^- 0.136
Ne 0.070
Na 0.192
Na^+ 0.095
Mg 0.160
Mg^{2+} 0.065
Al 0.143
Si 0.117
P 0.110
S 0.104
S^{2-} 0.184
Cl 0.099
Cl^- 0.181
Ar 0.098
K 0.238
K^+ 0.133
Ca 0.197
Ca^{2+} 0.099
Sc 0.160
Ti 0.147
V 0.136
Cr 0.128
Mn 0.118
Fe 0.124
Co 0.125
Ni 0.125
Cu 0.128
Zn 0.137
Ga 0.135
Ge 0.139
As 0.125
Se 0.116
Se^{2-} 0.198
Br 0.119
Br^- 0.195
Kr 0.112
Rb 0.251
Rb^+ 0.148
Sr 0.215
Sr^{2+} 0.113
Y 0.181
Zr 0.160
Nb 0.147
Mo 0.140
Tc 0.127
Ru 0.125
Rh 0.134
Pd 0.137
Ag 0.144
Cd 0.148
In 0.144
Sn 0.158
Sb 0.138
Te 0.143
Te^{2-} 0.221
I 0.136
I^- 0.216
Xe 0.131
Cs 0.270
Cs^+ 0.169
Ba 0.217
Ba^{2+} 0.135
Lu 0.173
Hf 0.144
Ta 0.143
W 0.141
Re 0.138
Os 0.135
Ir 0.135
Pt 0.139
Au 0.144
Hg 0.155
Tl 0.171
Pb 0.175
Bi 0.182
Po
At
Rn 0.140

Figure 2.11
The atomic and ionic size variations in the periodic table.

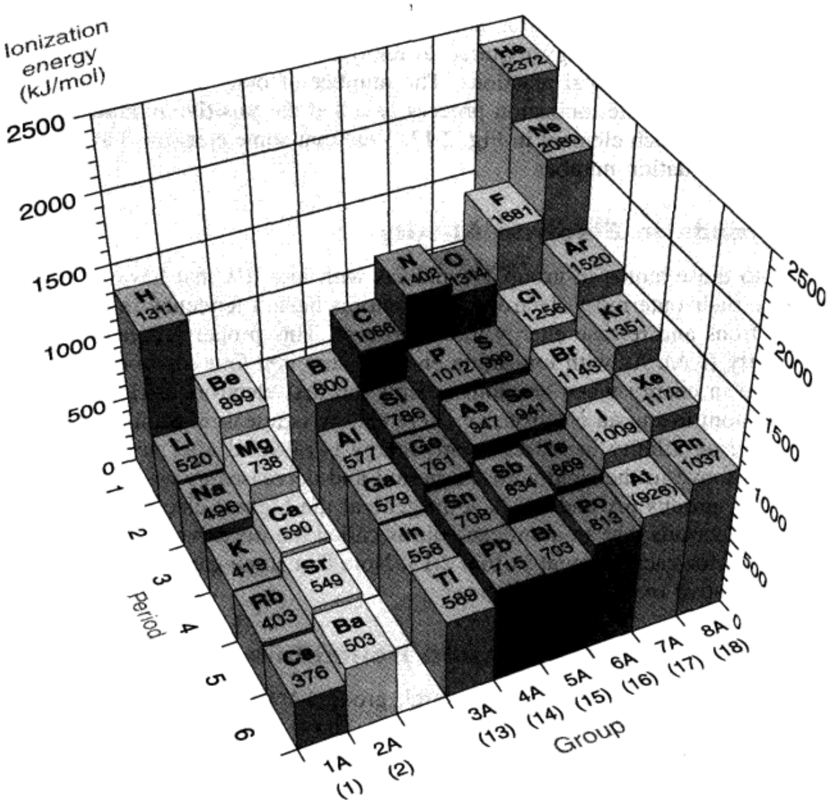


Figure 2.12
The ionization energy variations in the periodic table.

energy increases. We can therefore generalize that group 1A and 2A elements are highly susceptible to ionization. Conversely as the atomic size increases, moving down in a group, the distance between the nucleus and the outermost electrons increases, resulting in lower attraction forces between them; this will lower the energy required for the removal of electrons and thus the ionization energy.

For many electron atoms, as the first outer core electron is removed, it takes more energy to remove a second outer core electron; this indicates that the **second ionization energy,** IE2, will be higher. The increase in energy for successive electron removal will be exceptionally large when the outer core electrons are completely removed and what remain are the inner core electrons. For instance, the Li atom has one outer core electron, $2s^1$, and two inner core electrons, $1s^1$ and $1s^2$. When successively removing electrons, it takes 0.52 MJ/mole to remove the $2s^1$ electron, 7.30 MJ/mole for the $1s^2$ electron, and 11.81 MJ/mole for the $1s^1$ electron. Because of the higher levels of energy required to remove the inner core electrons, they are rarely involved in chemical reactions. The number of outer electrons that an atom can give up through the ionization process is called the **positive oxidation number** and is shown for each element in Fig. 2.13. Note that some elements have more than one positive oxidation number.

2.4.3 Trends in Electron Affinity

Contrary to those atoms in group 1A and 2A with low IE1 that have a tendency to easily lose their outermost electrons, some atoms have a tendency to accept one or more electrons and release energy in the process. This property is named the **electron affinity (EA).** As with ionization energy, there is a *first electron affinity*, EA1. The change in energy when an atom accepts the first electron, EA1, is opposite to that of an atom losing an electron, i.e., here energy is released. Similar to ionization energy, electron affinity increases (more energy is released after accepting an electron) as we move to the right across a period and decreases as we move down in a group. Thus, groups 6A and 7A have in general the highest electron affinities. The number of electrons that an atom can gain is called the **negative oxidation number** and is shown for each element in Fig. 2.13. Note that some elements have both positive and negative oxidation numbers.

2.4.4 Metals, Metalloids, and Nonmetals

Notwithstanding the exceptions, in general, group 1A and 2A atoms have low ionization energies and little to no electron affinity. These elements, called **reactive metals** (or simply metals), are electropositive, meaning that they have the natural tendency of losing electrons and in the process form cations (a positively charged ion forming as a result of losing an electron with its negative charge). The group 6A and 7A elements have a high ionization energy and very high electron affinity. These elements, called **reactive nonmetals** (or simply nonmetals), are electronegative, meaning that they have the natural tendency of accepting electrons and in the process form anions (a negatively charged ion forming as a result of accepting an electron with its negative charge).

In group 3A, the first element, boron, can behave either in a metallic or a nonmetallic manner. Such elements are called **metalloids.** The remaining members are all metals. In group 4A, the first member carbon and the next two members, silicon and germanium, are metalloids while the remaining elements, tin and lead, are metals. In group 5A, nitrogen and phosphorous are nonmetals, arsenic and antimony are metalloids, and finally bismuth is a metal. Thus, elements in groups 3A through 5A can behave in a variety of manners, but it is clear that as we move down in a group, the metallic behavior dominates; as we move right in a period, the nonmetallic behavior dominates. These various characteristics are well represented by the **electronegativity** of atoms indicating the degree by which they attract electrons to themselves (Fig. 2.14). In this figure, the electronegativity of

	2A	3B		4B	5B	6B	7B		8B		1B	2B	3A	4A	5A	6A		
1 **H** +1 −1																	1 **H** +1 −1	2 **He**
3 **Li** +1	4 **Be** +2												5 **B** +3	6 **C** +4 +2 −4	7 **N** +5 +4 +3 +2 +1 −3	8 **O** −1 −2	**F** −1	**Ne**
11 **Na** +1	12 **Mg** +2												13 **Al** +3	14 **Si** +4 −4	15 **P** +5 +3 −3	16 **S** +6 +4 +2 −2	17 **Cl** +7 +5 +3 +1 −1	18 **Ar**
19 **K** +1	20 **Ca** +2	21 **Sc** +3		22 **Ti** +4 +3 +2	23 **V** +5 +4 +3 +2	24 **Cr** +6 +3 +2	25 **Mn** +7 +6 +4 +3 +2	26 **Fe** +3 +2	27 **Co** +3 +2	28 **Ni** +2	29 **Cu** +2 +1	30 **Zn** +2	31 **Ga** +3	32 **Ge** +4 −4	33 **As** +5 +3 −3	34 **Se** +6 +4 −2	35 **Br** +5 +3 +1 −1	36 **Kr** +4 +2
37 **Rb** +1	38 **Sr** +2	39 **Y** +3		40 **Zr** +4	41 **Nb** +5 +4	42 **Mo** +6 +4 +3	43 **Tc** +7 +6 +4	44 **Ru** +8 +6 +4 +3	45 **Rh** +4 +3 +2	46 **Pd** +4 +2	47 **Ag** +1	48 **Cd** +2	49 **In** +3	50 **Sn** +4 +2	51 **Sb** +5 +3 −3	52 **Te** +6 +4 −2	53 **I** +7 +5 +3 +1 −1	54 **Xe** +6 +4 +2
55 **Cs** +1	56 **Ba** +2	57 **La** +3	58 → 71 **Ce** **Lu** +3	72 **Hf** +4	73 **Ta** +5	74 **W** +6 +4	75 **Re** +7 +6 +4	76 **Os** +8 +4	77 **Ir** +4 +3	78 **Pt** +4 +2	79 **Au** +3 +1	80 **Hg** +2 +1	81 **Tl** +3 +1	82 **Pb** +4 +2	83 **Bi** +5 +3	84 **Po** +2	85 **At** −1	86 **Rn**

Figure 2.13

The oxidation number variations in the periodic table.

(R.E. Davis, K.D. Gailey, and K.W. Whitten, Principles of Chemistry, Saunders College Publishing, 1984, p. 299.)

each atom is presented in a range of 0.8 to 4.0. As expected, nonmetals are more electronegative than metals while metalloids have intermediate electronegativities.

The atoms in group 8A are noble gases. They have very high ionization energy and no electron affinity. These elements are very stable and are the least reactive of all elements. With the exception of He, all remaining elements in this group (Ne, Ar, Kr, Xe, and Rn) have the s^2p^6 outer core electronic structure.

2.5 PRIMARY BONDS

The driving force behind the formation of bonds between atoms is that each atom seeks to be in the most stable state. Through bonding with other atoms, the potential energy of each bonding atom is lowered resulting in a more stable state. These bonds are called **primary bonds** and possess large interatomic forces.

We have already established that the behavior and characteristics of an atom, for instance, atomic size, ionization energy, and electron affinity, depend on its electronic structure and the attractive force between the nucleus and its electrons as well as the repulsive forces between electrons. Similarly, the behavior and properties of a mate-

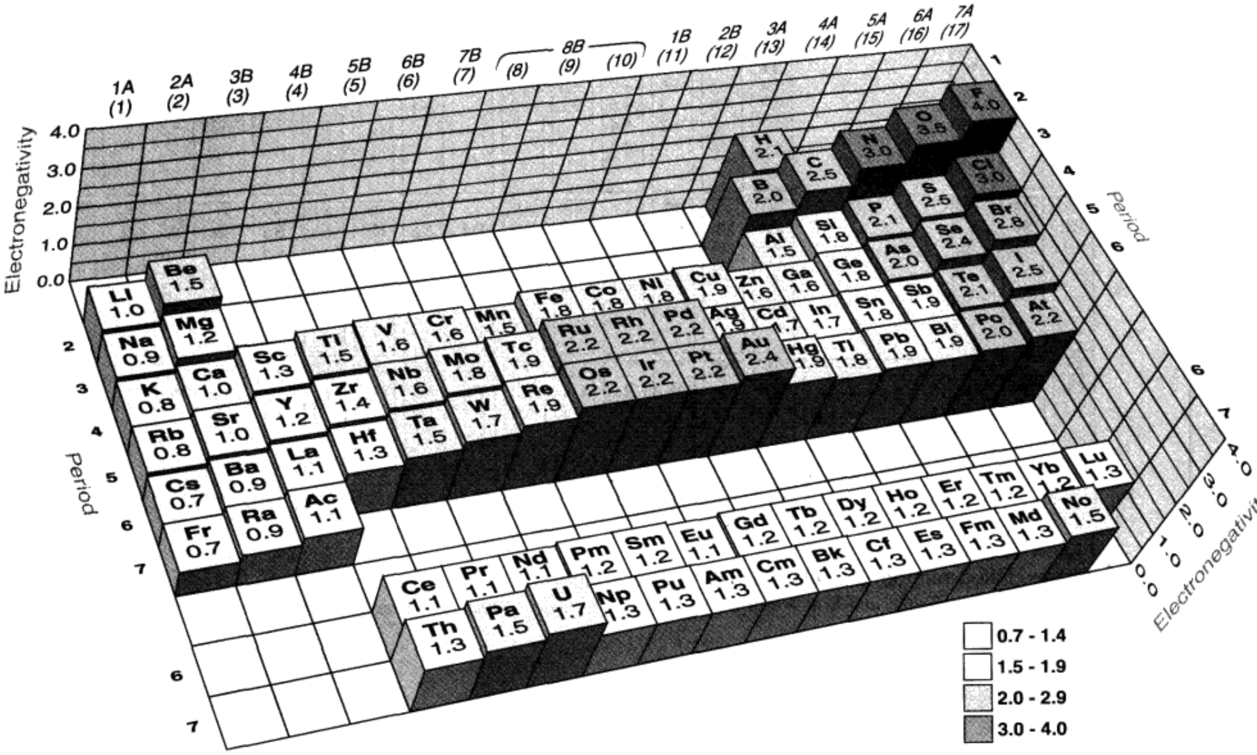


Figure 2.14
The electronegativity variations in the periodic table.

rial are directly dependent on the type and the strength of the bonds among its atoms. In the following sections, we will discuss the nature and characteristics of the existing primary and secondary bonds.

Recall that the elements in the periodic table can be classified into metals and nonmetals. The metalloids can behave either as a metal or as a nonmetal. There are three possible primary bonding combinations between the two types of atoms: (1) metal-nonmetal, (2) nonmetal-nonmetal, and (3) metal-metal.

2.5.1 Ionic Bonds

Electronic and Size Considerations Metals and nonmetals bond through electron transfer and **ionic bonding**. Ionic bonding is typically observed between atoms with large differences in their electronegativities (see Fig. 2.14); for instance, atoms of group 1A or 2A (reactive metals) with atoms of group 6A or 7A (reactive nonmetals). As an example, let us consider the ionic bonding between the metal Li with an electronegativity of 1.0 and the nonmetal F with an electronegativity of 4.0. In short, the Li atom loses an electron and forms a cation, Li^+. In this process, the radius decreases from $r = 0.157$ nm for the Li atom to $r = 0.060$ nm for the Li^+ cation. This reduction in size occurs because (1) after the ionization, the frontier electron is no longer in $n = 2$ but rather in $n = 1$ state and (2) the balance between the positive nucleus and the negative electron cloud is lost and the nucleus can exert a stronger force on the electrons, thus pulling them closer. Conversely, the F atom gains the electron lost by Li and forms an anion, F^-. In this case, the radius increases from $r = 0.071$ nm for the F atom to $r = 0.136$ nm for the F^-. It can be generalized that when a metal forms a cation, its radius reduces, and when a nonmetal forms an anion, its radius increases. The ionic sizes for various elements are given in Fig. 2.11. After the electron transfer process is completed, Li will have completed its outer electronic structure and takes on the structure of the noble gas He. Similarly, F will have completed its outer electronic structure and takes on the electronic structure of the noble gas Ne. The electrostatic attraction forces between the two ions will then hold the ions together to form an ionic bond. The ionic bonding process between Li and F is presented in electron configuration, orbital diagram, and electron dot formats in Fig. 2.15.

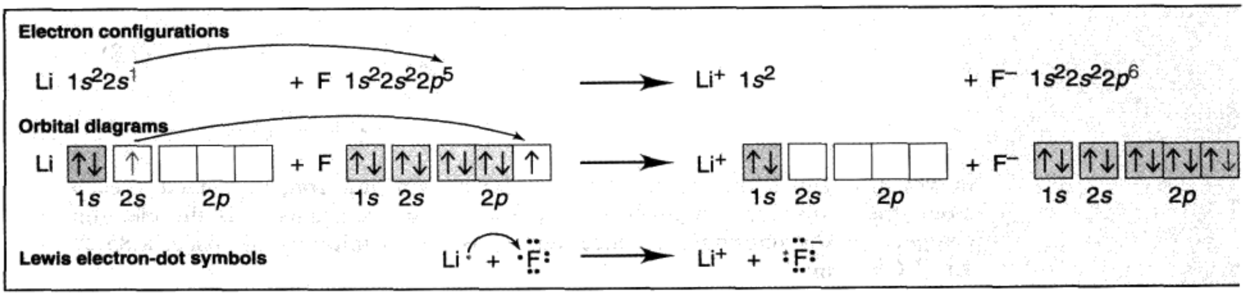


Figure 2.15
The ionic bonding process between Li and F. (*a*) Electron configuration presentation, (*b*) orbital diagram presentation, and (*c*) electron-dot symbol representation.

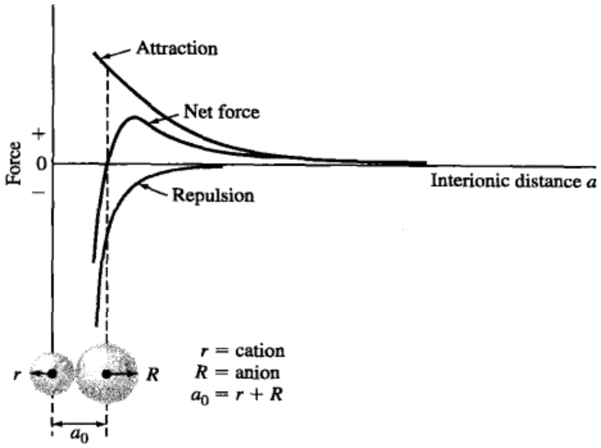


Figure 2.16
The attraction repulsion forces developed during ionic bonding.Note that net force is zero when the bond is formed.

Force Considerations From a force balance point of view, the positive nucleus of one ion will attract the negative charge cloud of the other ion and vise versa. As a result, the *interionic distance, a*, decreases, and they become closer. As the ions come closer, the negative electron charge clouds will interact and a repulsion force is developed. These two opposing forces will eventually balance each other to a net force of zero and that is when the **equilibrium interionic distance,** a_0, is reached and a bond is formed (Fig. 2.16).

The net force at any interionic distance may be calculated from the following equation.

$$F_{\text{net}} = \overset{\text{Attraction force}}{\boxed{-\frac{z_1 z_2 e^2}{4\pi\epsilon_0 a^2}}} - \underset{\text{Repulsion force}}{\boxed{\frac{nb}{a^{n+1}}}} \tag{2.8}$$

in which, z_1 and z_2 are the number of electrons removed from and added to each atom (they must have opposite signs), b and n are constants, e is the electron charge, a is the interionic distance, and ε_0 is the permittivity of space, 8.85×10^{-12} C²/N · m².

While the net force at equilibrium, when the bond is formed, is zero, the potential energy of the bond is at its lowest, E_{min} (Fig. 2.17).

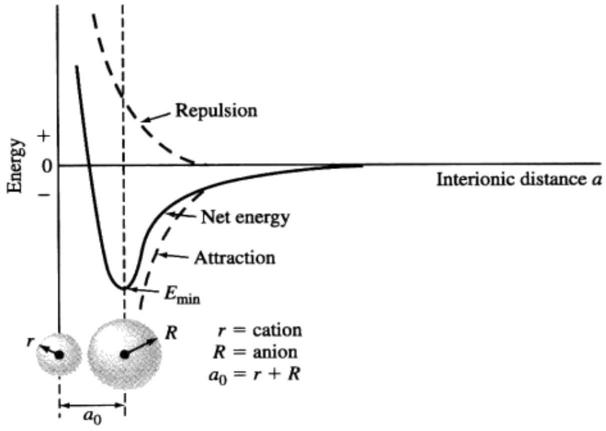

Repulsion
Energy
+
0
−
Interionic distance *a*
Net energy
Attraction
E_{min}
r
R
r = cation
R = anion
$a_0 = r + R$
a_0

Figure 2.17
The energy variations during ionic bonding. Note that the net energy is minimum when the bond is formed.

E_{min} may be determined using Eq. 2.8 and is negative, which indicates that if one wanted to break the bond, an amount of energy equal to E_{min} must be expended.

$$E_{net} = \overbrace{\boxed{\frac{z_1 z_2 e^2}{4\pi\epsilon_0 a}}}^{\text{Attraction force}} + \underbrace{\boxed{\frac{b}{a^n}}}_{\text{Repulsion force}} \tag{2.9}$$

EXAMPLE PROBLEM 2.7

If the attractive force between Mg^{2+} and S^{2-} ions at equilibrium is 1.49×10^{-9} N, calculate (a) the corresponding interionic distance. If S^{2-} ion has a radius of 0.184 nm, calculate (b) the ionic radius for Mg^{2+} and (c) the repulsion force between the two ions at this position.

■ Solution

The value of a_0, the sum of the Mg^{2+} and S^{2-} ionic radii, can be calculated from a rearranged form of Coulomb's law.

a.
$$a_0 = \sqrt{\frac{-Z_1 Z_2 e^2}{4\pi\epsilon_0 F_{attraction}}}$$

$$Z_1 = +2 \text{ for } \mathrm{Mg}^{2+} \qquad Z_2 = -2 \text{ for } \mathrm{S}^{2-}$$

$$|e| = 1.60 \times 10^{-19}\ \mathrm{C} \quad \epsilon_0 = 8.85 \times 10^{-12}\ \mathrm{C}^2/(\mathrm{N}\cdot\mathrm{m}^2)$$

$$F_{\text{attractive}} = 1.49 \times 10^{-9}\ \mathrm{N}$$

Thus,

$$a_0 = \sqrt{\frac{-(2)(-2)(1.60 \times 10^{-19}\ \mathrm{C})^2}{4\pi[8.85 \times 10^{-12}\ \mathrm{C}^2/(\mathrm{N}\cdot\mathrm{m}^2)](1.49 \times 10^{-8}\ \mathrm{N})}}$$

$$= 2.49 \times 10^{-10}\ \mathrm{m} = 0.249\ \mathrm{nm}$$

b. $a_0 = r_{\mathrm{Mg}^{2+}} + r_{\mathrm{S}^{2-}}$

or

$$0.249\ \mathrm{nm} = r_{\mathrm{Mg}^{2+}} + 0.184\ \mathrm{nm}$$

$$r_{\mathrm{Mg}^{2+}} = 0.065\ \mathrm{nm} \blacktriangleleft$$

EXAMPLE PROBLEM 2.8

The repulsion force between Na^+ (r = 0.095 nm) and Cl^- (r = 0.181) ions at equilibrium is -3.02×10^{-9} N. Calculate (a) the value of constant b using the repulsive force section of Eq. 2.8, and (b) the bonding energy, $E_{\min}$. Assume $n = 9$.

■ Solution

a. To determine the b value for a NaCl ion pair,

$$F = -\frac{nb}{a^{n+1}} \tag{2.6}$$

The repulsive force between a $\mathrm{Na}^+\mathrm{Cl}^-$ ion pair is -3.02×10^{-9} N. Thus,

$$-3.02 \times 10^{-9}\ \mathrm{N} = \frac{-9b}{(2.76 \times 10^{-10}\ \mathrm{m})^{10}}$$

$$b = 8.59 \times 10^{-106}\ \mathrm{N}\cdot\mathrm{m}^{10} \blacktriangleleft$$

b. To calculate the potential energy of the $\mathrm{Na}^+\mathrm{Cl}^-$ ion pair,

$$E_{\mathrm{Na}^+\mathrm{Cl}^-} = \frac{+Z_1Z_2e^2}{4\pi\epsilon_0 a} + \frac{b}{a^n}$$

$$= \frac{(+1)(-1)(1.60 \times 10^{-19}\ \mathrm{C})^2}{4\pi[8.85 \times 10^{-12}\ \mathrm{C}^2/(\mathrm{N}\cdot\mathrm{m}^2)](2.76 \times 10^{-10}\ \mathrm{m})} + \frac{8.59 \times 10^{-106}\ \mathrm{N}\cdot\mathrm{m}^{10}}{(2.76 \times 10^{-10}\ \mathrm{m})^9}$$

$$= -8.34 \times 10^{-19}\ \mathrm{J}^* + 0.92 \times 10^{-19}\ \mathrm{J}^*$$

$$= -7.42 \times 10^{-19}\ \mathrm{J} \blacktriangleleft$$

---

*1J = 1N·m

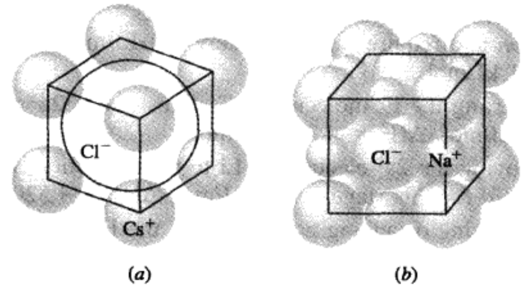


Figure 2.18
The ionic arrangement in two ionic solids:
(*a*) CsCl and (*b*) NaCl.

(After C.R. Barrett, W.D. Nix, and A.S. Tetelman, "The Principles of Engineering Materials," Prentice-Hall, 1973, p. 27.)

Ion Arrangement in Ionic Solids Although in the previous discussions, we focused on a pair of ions, an anion attracts cations from all directions and bonds with as many of these cations as possible. Alternatively, a cation attracts anions from all directions and bonds with as many of them as possible. This, in part, determines the ionic packing arrangement, and it is how the three-dimensional structure of the ionic solid is formed. Thus, when ions pack, they do so in a 3-D manner, with no preferred orientation (no separate single molecules exist), and as a result, the bonds are called *nondirectional* bonds.

The number of cations that can pack around an anion (packing efficiency) is determined by two factors: (1) their relative sizes and (2) charge neutrality. Consider CsCl and NaCl ionic solids. In the case of CsCl, eight Cl^- anions ($r = 0.181$ nm) pack around a central Cs^+ cation ($r = 0.169$ nm) as shown in Fig. 2.18*a*. Conversely, in case of NaCl, only six Cl^- anions, pack around a central Na^+ cation ($r = 0.095$ nm) as shown in Fig. 2.18*b*. In CsCl, the ratio of the radius of cation to anion $r_{Cs+}/ r_{Cl+} = 0.169/0.181 = 0.93$. The same ratio for NaCl is $0.095/0.181 = 0.525$. Thus, as the ratio of cation to anion radii decreases, fewer anions can surround a cation.

Electrical neutrality is the second contributing factor. For instance, in NaCl ionic solid, for every one Na^+ ion there must be one Cl^- ion in the overall solid. However, in CaF_2, for every Ca^{++} cation, there must be two F^- anions.

Energy Considerations in Ionic Solids To understand the energy considerations in ionic solid formation, consider the LiF ionic solid. Production of LiF ionic solid will result in the release of about 617 kJ/mol or in other words the *heat of formation* for LiF is $\Delta H^\circ = -617$ kJ/mol. However, the bonding process from the ionization stage to formation of an ionic solid can be divided into five steps, and some of these steps will require expending energy.

Step 1 Converting solid Li to gaseous Li ($1s^22s^1$): This step is called *atomization* and requires approximately 161 kJ/mol of energy, $\Delta H^1 = +161$ kJ/mol.

Step 2 Converting the F_2 molecule to F atoms ($1s^22s^12p^5$): This step requires 79.5 kJ/mol, $\Delta H^2 = +79.5$ kJ/mol.

Step 3 Removing the $2s^1$ electron of Li to form a cation, Li^+: The energy required for this stage is 520 kJ/mol, $\Delta H^3 = +520$ kJ/mol.

Step 4 Transferring or adding an electron to the F atom to form an anion, F^-: This process actually releases energy. Therefore, the change in energy is designated as negative and is approximately -328 kJ/mol, $\Delta H^4 = -328$ kJ/mol.

Step 5 Formation of an ionic solid from gaseous ions. The electrostatic attraction forces between cations and anions will produce ionic bonds between gaseous ions to form a three-dimensional solid. The energy associated with this process is called the **lattice energy** and is unknown, $\Delta H^5 = ?$ kJ/mol.

According to the **Hess law,** the total heat of formation of LiF should be equal to the sum of the heat of formations required in each step. In other words,

$$\Delta H^0 = \Delta H^1 + \Delta H^2 + \Delta H^3 + \Delta H^4 + \Delta H^5 \qquad \textbf{(2.11)}$$

From this relationship, we can determine the magnitude of the lattice energy, $\Delta H^5 = \Delta H^0 - [\Delta H^1 + \Delta H^2 + \Delta H^3 + \Delta H^4] = -617\text{ kJ} - [161\text{ kJ} + 79.5\text{ kJ} + 520\text{ kJ} - 328\text{ kJ}] = -1050$ kJ. This means that although energy is expended in steps 1, 2, and 3, a greater amount of lattice energy is produced during the ionic solid formation phase (1050 kJ). In other words, the energy expended for steps 1, 2, and 3 is supplied and exceeded by the lattice energy produced in step 5 when ions are attracted to form a solid. This verifies the concept that atoms form bonds to lower their potential energies. The lattice energies associated with various ionic solids are given in Table 2.5. Examination of the table shows that (1) lattice energies decrease as we move down in groups or as the size of the ion increases and (2) lattice energies significantly increase when the ions involved have higher ionic charge.

Table 2.5 The lattice energy and melting point values for various ionic solids

Ionic solid	Lattice energy* kJ/mol	kcal/mol	Melting point (°C)
LiCl	829	198	613
NaCl	766	183	801
KCl	686	164	776
RbCl	670	160	715
CsCl	649	155	646
MgO	3932	940	2800
CaO	3583	846	2580
SrO	3311	791	2430
BaO	3127	747	1923

*All values are negative for bond formation (energy is released).

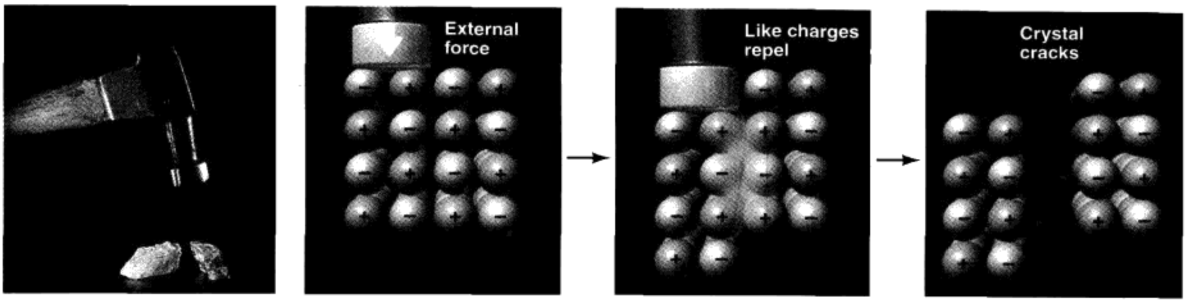


Figure 2.19
The fracture mechanism of ionic solids. The blow will force like ions to face each other and produce large repulsive forces. The large repulsive forces can fracture the material.
(© The McGraw-Hill Higher Education/Stephen Frisch, photographer.)

Ionic Bonds and Material Properties Ionic solids generally have high melting temperatures. It is observed in Table 2.5 that as the lattice energy of ionic solid increases, its melting temperature also increases as evidenced in MgO with the highest lattice energy of 3932 kJ/mol and highest melt temperature of 2800°C. In addition, ionic solids are generally hard (do not dent), rigid (do not bend or do not have any springiness), strong (hard to break), and brittle (deform little before fracture). These properties of ionic solids are due to the strong electrostatic forces that hold the ions together. Note in Figs. 2.18 and 2.19 that anions and cations alternate in their positioning. If large forces are applied to ionic solids, it could force a shift in the positioning that would put like ions against each other. This will create a large repulsive force that would fracture the solid (Fig. 2.19).

Finally, generally speaking, ionic solids do not conduct electricity well and are therefore excellent insulators. The reason for this is that electrons are tightly held inside the bond and cannot participate in the conduction process. However, when melted or dissolved in water, ionic materials can conduct electricity through ionic diffusion (movement of ions). This is also evidence that ions are in fact present in the solid state.

2.5.2 Covalent Bonds

Shared Electron Pairs and Bond Order **Covalent bonding** is typically observed between atoms with small differences in their electronegativities and mostly between nonmetals. Nonmetal atoms bond through localized sharing of electrons and covalent bonding. Covalent bonding is the most common form of bonding in nature ranging from diatomic hydrogen to biological materials to synthetic macromolecules. This type of bond can also form as a percentage of total bonds in ionic as well as metallic materials. Similar to ionic bonds, covalent bonds are also very strong.

Consider the covalent bond between two hydrogen atoms. At first, the nucleus of one H atom attracts the electron cloud of the other; the atoms get closer to each other. As they get close, the two electron clouds interact and both atoms start to take ownership of both electrons (share electrons). The atoms keep getting closer until they reach the equilibrium point in which the two H atoms will form a bond by sharing their electrons, both completing their outer electronic structure, and reaching the

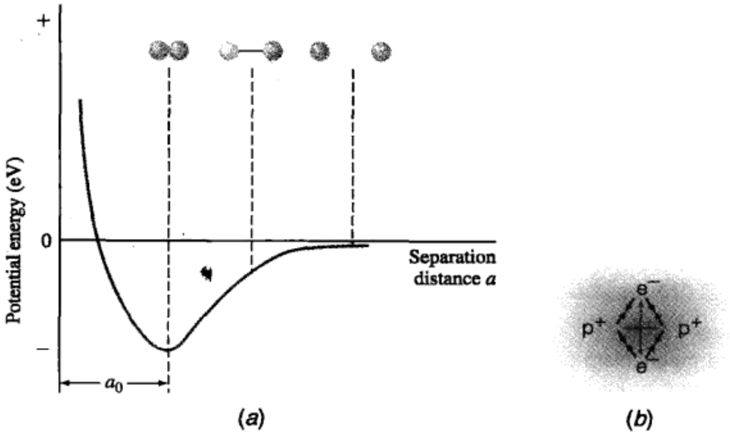


Figure 2.20
Covalent bonding between hydrogen atoms. (*a*) The potential energy diagram and (*b*) schematic showing the H_2 molecule and the intramolecular forces. Note that the electrons can exist at any location within the diagram; however we have chosen to show them in these locations for ease of force analysis.

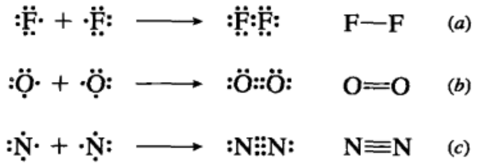


Figure 2.21
The Lewis electron dot representation for (*a*) F_2, bond order of 1, (*b*) O_2, bond order of 2, and (*c*) N_2, bond order of 3.

lowest state of energy, as shown in Fig. 2.20*a*. In this position, the attraction forces are balanced against repulsion forces, Fig. 2.20*b*. In this figure, the electrons are shown in the given positions for clarity of explanation. In reality, the electrons can be located at any point within the shaded area.

The covalent bonding between atoms is crudely represented by the *Lewis electron dot* representation. The electron dot representation for the covalent bonds in F_2, O_2, and N_2 is presented in Fig. 2.21. In this figure, the pair of electrons in the formed bond, called the **shared pair** or **bonding pair,** is either represented by a pair of dots or a line. It is important to note that the atoms will form as many shared pairs as needed to complete their outer electronic structure (8 electrons total). Therefore, F atoms ($2s^22p^5$) will form one shared pair resulting in a **bond order** of one, O atoms ($2s^22p^4$) will form two shared pairs (bond order of two), and N ($2s^22p^3$) atoms will form three shared pairs (bond order of three). The strength of a covalent bond

Table 2.6 The bond energy and bond lengths for various covalent bonds

	Bond energy*		
Bond	**kcal/mol**	**kJ/mol**	**Bond length (nm)**
C—C	88	370	0.154
C=C	162	680	0.13
C≡C	213	890	0.12
C—H	104	435	0.11
C—N	73	305	0.15
C—O	86	360	0.14
C=O	128	535	0.12
C—F	108	450	0.14
C—Cl	81	340	0.18
O—H	119	500	0.10
O—O	52	220	0.15
O—Si	90	375	0.16
N—O	60	250	0.12
N—H	103	430	0.10
F—F	38	160	0.14
H—H	104	435	0.074

*Approximate values since environment changes energy. All values are negative for bond formation (energy is released).

Source: L.H. Van Vlack, "Elements of Materials Science," 4th ed., Addison-Wesley, 1980.

depends on the magnitude of the attraction force between the nuclei and the number of shared pairs of electrons. The energy required to overcome this attraction force is called the **bond energy.** Bond energy will depend on the bonded atoms, electron configurations, nuclear charges, and the atomic radii. Therefore each type of bond has its own bond energy.

It is also important to note that unlike the Lewis dot-representation of the covalent molecule, the bonding electrons do not stay in fixed position between atoms. However, there is a higher probability of finding them in the area between the bonded atoms, Fig. 2.20*b*. Unlike ionic bonds, covalent bonds are *directional* and the shape of the molecule is not necessarily conveyed by the dot-representation; a majority of these molecules possess complex three-dimensional shapes with non-orthogonal bond angles. Finally, the number of neighbors (or packing efficiency) around an atom will depend on the bond order.

Bond Length, Bond Order, and Bond Energy A covalent bond has a **bond length** that is the distance between the nuclei of two bonded atoms at the point of minimum energy. There exists a close relationship among bond order, bond length, and bond energy: for a given pair of atoms, with higher bond order, the bond length will decrease; and as bond length decreases, bond energy will increase. This is because the attraction force is strong between the nuclei and the multiple shared pairs. The bond energies and length between selected atoms with different bond orders are given in Table 2.6.

The relationship between bond length and bond energy can be extended by considering situations where one atom in the bond remains constant and the other varies. For instance, the bond length of C–I is greater than C–Br is greater than C–Cl. Note that bond length increases as the diameter of the atom bonding with C increases (diameter of I > Br > Cl). Thus, the bond energy will be greatest in C–Cl, lower in C–Br, and lowest in C–I.

Nonpolar and Polar Covalent Bonds Depending on the differences in electronegativities between the bonding atoms, a covalent bond could be either polar or nonpolar (to various degrees). Examples of a nonpolar covalent bond are H_2, F_2, N_2 and other covalent bonds between atoms of similar electronegativities. In these bonds, the sharing of the bonding electrons is equal between the atoms and the bonds are therefore *nonpolar*. On the other hand, as the difference in electronegativities between the covalently bonding atoms increases, for instance in HF, the sharing of the bonding electrons is unequal (the bonding electrons displace toward the more electronegative atom). This produces a *polar covalent bond*. As the difference in electronegativity increases, the polarity of the bond increases, and if the difference becomes large enough, the bond becomes ionic. For instance, F_2, HBr, HF, and NaF will have, respectively, nonpolar covalent, polar covalent, highly polar covalent, and ionic types of bond.

Covalent Bonding in Carbon-Containing Molecules In the study of engineering materials, carbon is very important since it is the basic element in most polymeric materials. The carbon atom in the ground state has the electron configuration $1s^2 2s^2 2p^2$. This electron arrangement indicates that carbon should form *two covalent bonds* with its two half-filled 2p orbitals. However, in many cases, carbon forms *four covalent bonds* of equal strength. The explanation for the four carbon covalent bonds is provided by the concept of *hybridization* whereby upon bonding, one of the 2s electrons is promoted to a 2p orbital so that *four equivalent* sp^3 **hybrid orbitals** are produced, as indicated in the orbital diagrams of Fig. 2.22. Even though energy is required to promote the 2s electron to the 2p state in the hybridization process, the energy necessary for the promotion is more than compensated for by the decrease in energy accompanying the bonding process.

Carbon in the form of diamond exhibits sp^3 tetrahedral covalent bonding. The four sp^3 hybrid orbitals are directed symmetrically toward the corners of a regular tetrahedron, as shown in Fig. 2.23. The structure of diamond consists of a massive

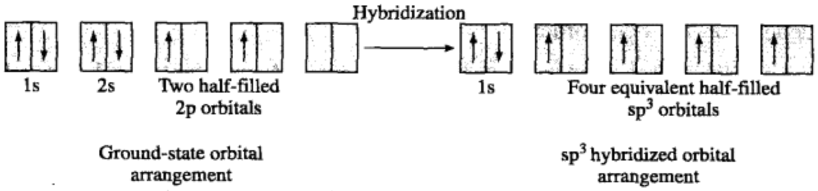

Hybridization
1s
2s
Two half-filled 2p orbitals
1s
Four equivalent half-filled sp³ orbitals
Ground-state orbital arrangement
sp³ hybridized orbital arrangement

Figure 2.22
The hybridization of carbon orbitals for formation of single bonds.

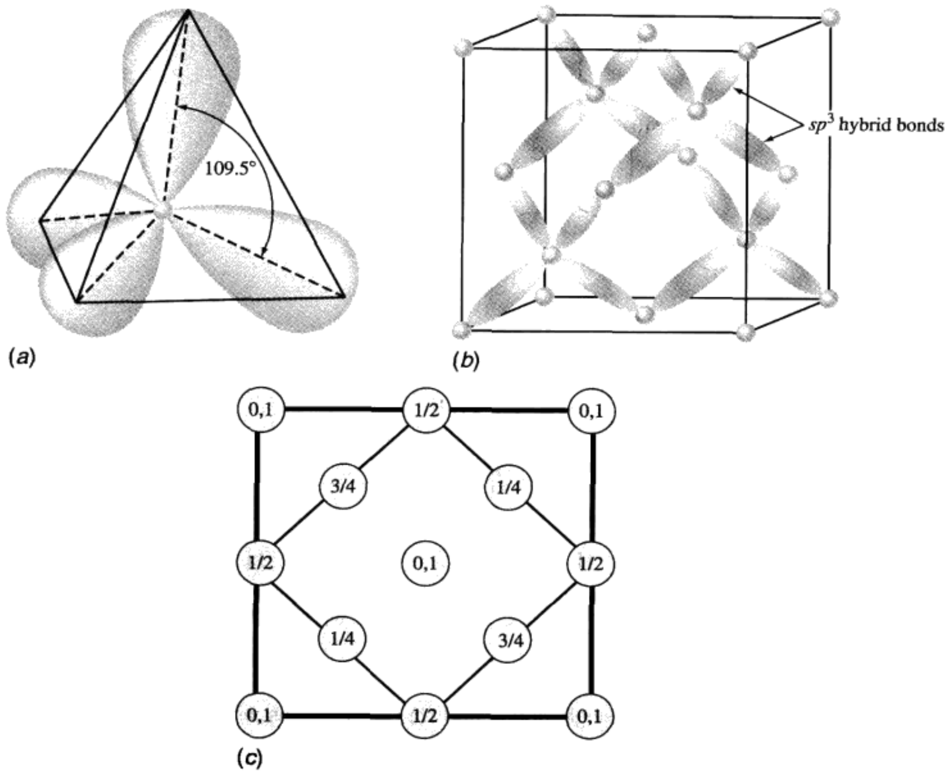


Figure 2.23
(*a*) The angle between the symmetric hybridized sp^3 orbitals in a carbon atom. (*b*) Tetrahedral sp^3 covalent bonds in diamond called the diamond cubic structure. Each shaded region represents a shared pair of electrons. (*c*) The z location of each carbon atom is shown in the basal plane. The notation "0, 1" means there is one atom at $z = 0$, and one atom at $z = 1$.

network with sp^3 tetrahedral covalent bonding, as shown in Fig. 2.23. This structure accounts for the extremely high hardness of diamond and its high bond strength and melting temperature. Diamond has a bond energy of 711 kJ/mol (170 kcal/mol) and a melting temperature of 3550°C.

Covalent Bonding in Hydrocarbons Covalently bonded molecules containing only carbon and hydrogen are called *hydrocarbons*. The simplest hydrocarbon is methane in which carbon forms four sp^3 tetrahedral covalent bonds with hydrogen atoms, as shown in Fig. 2.24. The intramolecular bonding energy of methane is relatively high at 1650 kJ/mol (396 kcal/mol), but the intermolecular bond energy is very low at about 8 kJ/mol (2kcal/mol). Thus, the methane molecules are very weakly bonded together, resulting in a low melting point of −183 °C.

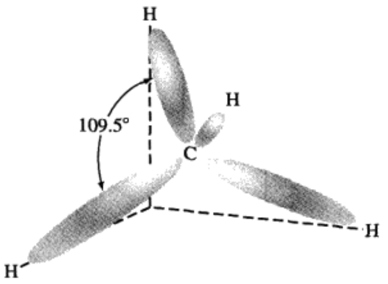


Figure 2.24
The methane molecule with four tetrahedral sp^3 bonds.

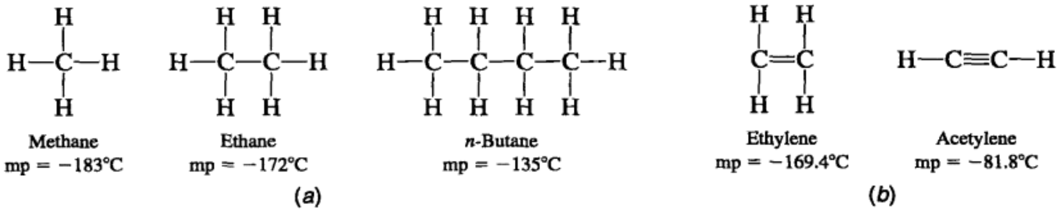


Figure 2.25
Structural formulas for (*a*) hydrocarbons with single bonds and (*b*) hydrocarbons with multiple bonds.

Fig. 2.25*a* shows structural formulas for methane, ethane, and normal (*n*−) butane, which are single covalently bonded, volatile hydrocarbons. As the molecular mass of the molecule increases, so does its stability and melting point.

Carbon can also bond itself to form double and triple bonds in molecules as indicated in the structural formulas for ethylene and acetylene shown in Fig. 2.25*b*. Double and triple carbon-carbon bonds are chemically more reactive than single carbon-carbon bonds. Multiple carbon-carbon bonds in carbon-containing molecules are referred to as *unsaturated bonds*.

An important molecular structure for some polymeric materials is the benzene structure. The benzene molecule has the chemical composition C_6H_6 with the carbon atoms forming a hexagonal-shaped ring referred to sometimes as the *benzene ring* (Fig. 2.26). The six hydrogen atoms of benzene are covalently bonded with single bonds to the six carbon atoms of the ring. However, the bonding arrangement between the carbon atoms in the ring is complex. The simplest way of satisfying the requirement that each carbon atom have four covalent bonds is to assign alternating single and double bonds to the carbon atoms in the ring itself (Fig. 2.26*a*). This structure can be represented more simply by omitting the external hydrogen atoms

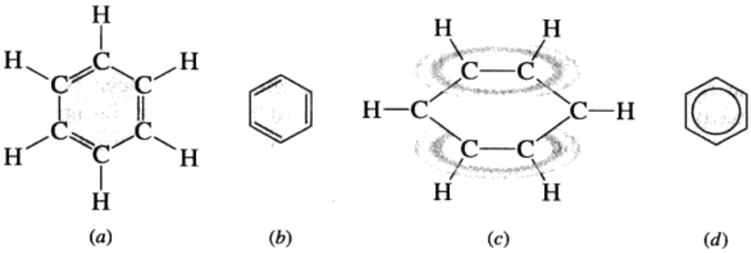


Figure 2.26
Structural formulas for benzene (*a*) using straight line bonding notation and (*b*) simplified notation of (*a*). (*c*) Bonding arrangement showing the delocalization of the carbon-carbon electrons within the ring, and (*d*) simplified notation of (*c*).

(Fig. 2.26*b*). This structural formula for benzene will be used in this book since it more clearly indicates the bonding arrangement in benzene.

However, experimental evidence indicates that a normal reactive double carbon-carbon bond does not exit in benzene and that the bonding electrons within the benzene ring are delocalized, forming an overall bonding structure intermediate in chemical reactivity to that between single and double carbon-carbon bonds (Fig. 2.26*c*). Thus, most chemistry books are written using a circle inside a hexagon to represent the structure of benzene (Fig. 2.26*d*).

Covalent Bonds and Material Properties Materials that consist of covalent bonds are numerous: most gas molecules, liquid molecules, and low-melting solid molecules are formed through covalent bonds. Also, what is common among these materials is that they are molecular (the bond between molecules is weak). The covalent bonds between the atoms are very strong and are difficult to break; however, the bond between molecules is weak and breaks easily. Therefore, such materials boil or melt very easily. We will cover the nature of these bonds in future sections.

In contrast to the above molecular materials, in some materials called **network covalent solids** (no molecules), all the bonds are covalent. In such materials, the number of neighbors for an atom depends on the number of covalent bonds available as per the bond order. Two examples of such covalent solids are quartz and diamond. The properties of quartz reflect the strength of the covalent bonds in it. Quartz is made up of Si and O atoms (SiO_2) continuously connected to each other through covalent bonds in a 3-D network. There are no molecules in this material. Similar to diamond, quartz is very hard and melts at a high temperature of 1550°C. The high melting point of network covalent solids is a reflection of the high bonding energies and the true strength of covalent bonds. Covalent materials are poor conductors of electricity not only in a network solid form but also in a liquid or molten form. This is because electrons are tightly bonded in the shared pairs, and no ions are available for charge transport.

2.5.3 Metallic Bonds

Although two isolated metal atoms may form strong covalent bonds between atoms (Na_2), the resulting material will be gaseous, i.e. the bond between Na_2 molecules will be weak. The question is then, "What type of bond holds the atoms of solid sodium (or any other solid metal) together?" It is observed that during solidification, from a molten state, the atoms of a metal pack tightly together, in an organized and repeating manner, to lower their energy and achieve a more stable state in the form of a solid, thus creating **metallic bonds.** For instance in copper, each copper atom will have 12 neighbors packed around it in an orderly fashion (Fig. 2.27*a*). In the process, all the atoms contribute their valence electrons to a "sea of electrons" or the "electron charge cloud" (Fig. 2.27*b*). These valence electrons are delocalized, move freely in the sea of electrons, and do not belong to any specific atoms. For this reason, they are also called *free electrons*. The nuclei and the remaining core electrons of tightly packed atoms form a cationic or a positive core (because they have lost their valence electrons). What keeps the atoms together, in solid metals, is the attraction force between the positive ionic core (metal cations) and the negative electron cloud. This is referred to as *metallic bonding*.

The metallic bond is three-dimensional and nondirectional, similar to the ionic bond. However, since there are no anions involved, there are no electrical neutrality restrictions. Also, the metallic cations are not held in place as rigidly as they are in ionic solids. In contrast to the directional covalent bonds, there are no shared localized electron pairs between atoms; metallic bonds are therefore weaker than covalent bonds.

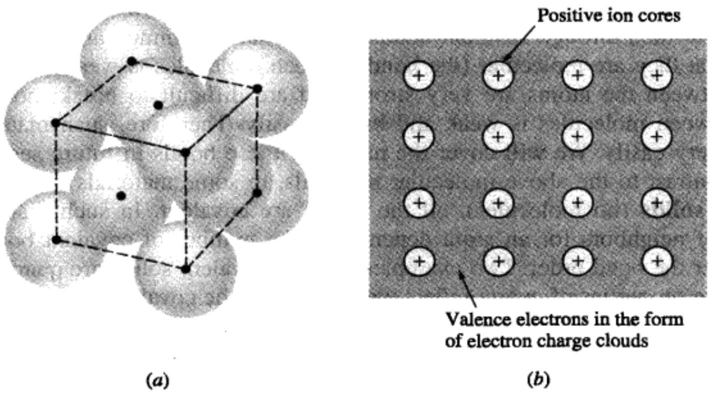


Figure 2.27
(*a*) The ordered, efficiently packed structure of copper atoms in a metallic solid. (*b*) The positive ion core and the surrounding sea of electrons model for metallic bonding.

Metallic Bonds and Material Properties The melting points of pure metals are only moderately high because, for melting, it is not required to break the bond between the ionic core and the electron cloud. Thus, on average, ionic materials and covalent networks have higher melting temperatures because they both require breakage of the bonds for melting. The bond energies and the melting point of metals vary greatly, depending on the number of valence electrons and the percent metallic bonding. In general, group 1A elements (alkali metals) have only one valence electron and possess almost exclusively metallic bonds. As a result, these metals have lower melt temperatures than group 2A elements that have two valence electrons and a higher percentage of covalent bonding.

The elements in the fourth period, including the transition metals, their outer electronic configurations, bond energies, and melt temperatures, are presented in Table 2.7. In metals, as the number of valence electrons increases, the attraction force between the positive core and the electron cloud also increases; K ($4s^1$) with one valence electron has a melt temperature of 63.5°C compared to considerably higher 851°C for Ca ($4s^2$) with two valence electrons (Table 2.7). With the introduction of 3d electrons in the transition metals, the number of valence electrons increases as does the melt temperature with a maximum of 1903°C for Cr ($3d^54s^1$). This increase in bonding energy and melt temperature in transition metals is attributed to an increase in the percentage of covalent bonding. As the 3d and 4s orbitals become full, the melt temperature again starts to drop among transition metals with the lowest of 1083°C for copper ($3d^{10}4s^1$). After Cu, there is an even more significant drop in melt temperature for Zn ($4s^2$) to 419°C.

The mechanical properties of metals are significantly different than those of ionic and covalent networked materials. Pure metals, specifically, are significantly more malleable (soft and deformable) than ionic or covalent networked materials. As a matter of fact, there is limited structural application for pure metals because of their softness. This is because, under the action of an external force, the ions in the metal

Table 2.7 Bonding energies, electron configurations, and melting points of the fourth-period metals of the periodic table

Element	Electron configuration	Bonding energy kJ/mol	Bonding energy kcal/mol	Melting point (°C)
K	$4s^1$	89.6	21.4	63.5
Ca	$4s^2$	177	42.2	851
Sc	$3d^14s^2$	342	82	1397
Ti	$3d^24s^2$	473	113	1660
V	$3d^34s^2$	515	123	1730
Cr	$3d^54s^1$	398	95	1903
Mn	$3d^54s^2$	279	66.7	1244
Fe	$3d^64s^2$	418	99.8	1535
Co	$3d^74s^2$	383	91.4	1490
Ni	$3d^84s^2$	423	101	1455
Cu	$3d^{10}4s^1$	339	81.1	1083
Zn	$4s^2$	131	31.2	419
Ga	$4s^24p^1$	272	65	29.8
Ge	$4s^24p^2$	377	90	960

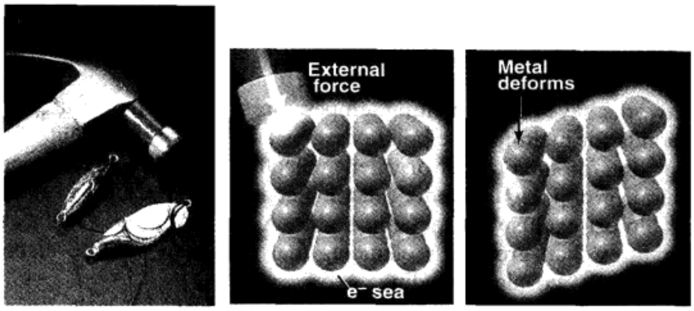


Figure 2.28
(*a*) The deformation behavior of metallic solids. (*b*) The blow will force the cations to slide past each other and thus allow great deal of malleability.
(The McGraw-Hill Higher Education/Stephen Frisch, photographer.)

can slip past each other with relative ease, Fig. 2.28. The bonds between the ions in a metal can be broken at lower energy levels compared to ionic and covalent bonds. Compare this behavior to that presented in Fig. 2.19 for ionic materials. In future chapters, we will explain how the strength of a pure metal can be significantly increased through alloying impurities, plastic deformation, grain refinement, and heat treatment.

The main utilization of pure metals is in electrical and electronic applications. Pure metals are excellent conductors of electricity because of the delocalized nature of the valence electrons. As soon as a metal component is placed in an electrical circuit, each valence electron will rather freely carry a negative charge module toward the positive electrode. This is impossible in ionic or covalent materials because the valence electrons are tightly held in place by the nuclei. Finally, metals are excellent conductors of heat because of the efficient transfer of thermal atomic vibrations across the metal.

2.5.4 Mixed Bonding

The chemical bonding of atoms or ions can involve more than one type of primary bond and can also involve secondary dipole bonds. For primary bonding there can be the following combinations of mixed-bond types: (1) ionic-covalent, (2) metallic-covalent, (3) metallic-ionic, and (4) ionic-covalent-metallic.

Ionic-Covalent Mixed Bonding Most covalent-bonded molecules have some ionic binding, and vice versa. The partial ionic character of covalent bonds can be interpreted in terms of the electronegativity scale of Fig. 2.14. The greater the difference in the electronegativities of the elements involved in a mixed ionic-covalent bond, the greater the degree of ionic character of the bond. Pauling proposed the following equation to determine the percentage ionic character of bonding in a compound AB:

$$\%\ \text{ionic character} = (1 - e^{(-1/4)(X_A - X_B)^2})\ (100\%) \qquad \textbf{(2.12)}$$

where X_A and X_B are the electronegativities of the atoms A and B in the compound, respectively.

Many semiconducting compounds have mixed ionic-covalent bonding. For example, GaAs is a 3–5 compound (Ga is in group 3A and As in group 5A of the