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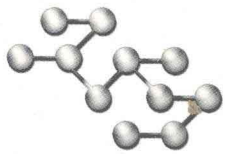
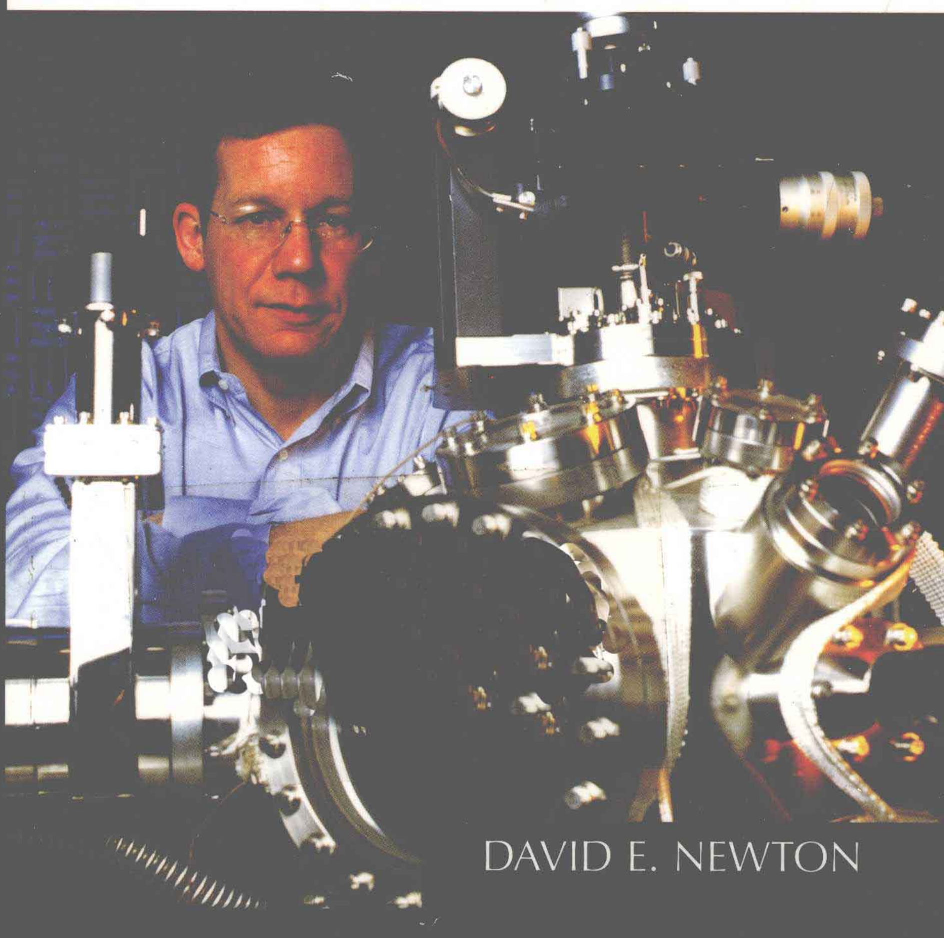
THE NEW CHEMISTRY

Chemistry of New Materials





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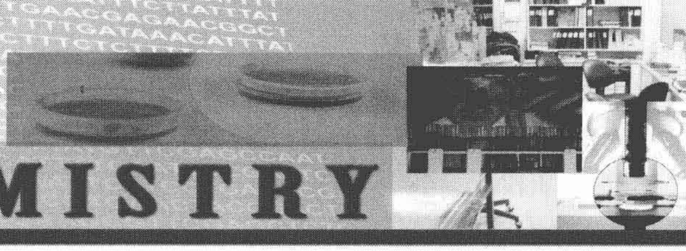

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Facts On File
An imprint of Infobase Publishing

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Facts On File, Inc.
An imprint of Infobase Publishing
132 West 31st Street
New York NY 10001

ISBN-10: 0-8160-5278-6
ISBN-13: 978-0-8160-5278-3

Library of Congress Cataloging-in-Publication Data
Newton, David E.
Chemistry of new materials / David E. Newton.
p. cm.—(New chemistry)
Includes bibliographical references and index.
ISBN 0-8160-5278-6
1. Materials—Popular works. 2. Chemistry, Technical—Popular works.
I. Title.
TA403.2.N49 2007
620.1'1—dc22 2006035943

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Text design by James Scotto-Lavino
Illustrations by Anja Tchepets
Project editing by Dorothy Cummings

Printed in the United States of America

MP CGI 10 9 8 7 6 5 4 3 2 1

This book is printed on acid-free paper.

One Last Time . . .
for

John McArdle, Lee Nolet, Richard Olson, David Parr,
David Rowand, Jeff Williams, and John D'Emilio

Thanks for the memories!

PREFACE

The subject matter covered in introductory chemistry classes at the middle and high school levels tends to be fairly traditional and relatively consistent from school to school. Topics that are typically covered in such classes include atomic theory, chemical periodicity, ionic and covalent compounds, equation writing, stoichiometry, and solutions. While these topics are essential for students planning to continue their studies in chemistry or the other sciences and teachers are correct in emphasizing their importance, they usually provide only a limited introduction to the rich and exciting character of research currently being conducted in the field of chemistry. Many students not planning to continue their studies in chemistry or the other sciences may benefit from information about areas of chemistry with immediate impact on their daily lives or of general intellectual interest. Indeed, science majors themselves may also benefit from the study of such subjects.

The New Chemistry is a set of six books intended to provide an overview of some areas of research not typically included in the beginning middle or high school curriculum in chemistry. The six books in the set—*Chemistry of Drugs, Chemistry of New Materials, Forensic Chemistry, Chemistry of the Environment, Food Chemistry,* and *Chemistry of Space*—are designed to provide a broad, general introduction to some fields of chemistry that are less commonly mentioned in standard introductory chemistry courses. They cover topics ranging from the most fundamental fields of chemistry, such as the origins of matter and of the universe, to those with important applications to everyday life, such as the composition of foods and drugs. The set title The New Chemistry has been selected to emphasize the extensive review of recent research and advances in each of the fields of chemistry covered in the set. The books in The New Chemistry set are written for middle school and high school readers. They assume some basic understanding of the principles of chemistry that are generally gained in an introductory middle or high school course in the subject. Every book contains a large amount of material that should be accessible to the interested reader with no more than an introductory understanding of chemistry and a smaller amount of material that may require a more advanced understanding of the subject.

The six books that make up the set are independent of each other. That is, readers may approach all of the books in any sequence whatsoever. To assist the reader in extending his or her understanding of each subject, each book in the set includes a glossary and a list of additional reading sources from both print and Internet sources. Short bibliographic sketches of important figures from each of the six fields are also included in the books.

INTRODUCTION

Nature has a remarkable variety of ways of assembling atoms and molecules to form natural products, and people still have a great deal to learn from these processes. But natural methods provide no more than a hint of the host of new products that can be made. These new products are changing—and will continue to change—the way in which scientists and engineers build the substances that make human civilization what it is today. *Chemistry of New Materials* reviews some of these exciting fields of materials research.

The level of a human civilization, it might be argued, is largely a function of the materials with which it has to work. Nature has provided a bountiful supply of materials, such as mud, stone, and wood. So humans have never suffered for lack of substances with which to build their homes, construct their boats, fashion their weapons, make their tools, design their kitchen implements, and produce the myriad other objects needed for everyday life.

Early on, people learned how to combine natural materials in a variety of ways to make them more useful. They found that the combination of mud and straw (bricks) was a stronger and more permanent building material than either material by itself. And, thus, one of the first *composite* materials was born. The importance of societies' ability to manipulate natural materials is evident in the fact that the earliest human civilizations have actually been named for the primary substances with which they worked: stone, iron, copper, and bronze.

Many of the new materials developed by early humans were modeled on substances found in nature. The first alloys, for example, were little more than artificial copies of substances produced when fire, lightning, or some other natural source of energy caused the fusion of naturally occurring materials on the Earth's surface. Over time, however, people learned how to modify these processes to produce new alloys and other materials that were superior to those found in nature. This pattern has dominated materials research since the dawn of time. Many of the best new materials available today were created when scientists discovered how nature makes its composites and found new and better ways to duplicate those processes. One of the most exciting fields of materials research today involves the development of new *biomaterials,* substances similar to naturally occurring products found in living organisms that can be used in a host of new ways by medical workers.

Perhaps the most promising field of materials research today aims to understand and imitate the way in which nature produces materials at its most fundamental level, that of atoms and molecules. The field of *nanotechnology* promises to revolutionize materials science in a way that has no precedent in human history. For the first time ever, scientists are learning how to construct new materials from the "bottom up," beginning with individual atoms and molecules, rather than from the "top down," as has always been the case in the past. This research promises not only to revolutionize existing fields of science and technology, such as computer science, but also to open up entirely new ways of thinking about, designing, and building synthetic materials.

Another field of materials science that has become identified with rapid and sometimes startling change is the development of so-called *smart materials*, materials that can sense changes in the surrounding environment and, in many cases, change their own character in response. Once no more than an optimistic dream of how materials *could* be used, smart materials have begun to appear in a virtually endless number of everyday applications, ranging from automotive airbags that protect riders with greater efficiency, to skis that "read" the snow and ice over which they travel and make appropriate adjustments in their shape, to concrete highways that measure the weight of trucks that pass over them.

Even in fields in which materials science had become somewhat routine and boring, such as the development of new *polymers,* unexpected and promising breakthroughs have occurred. The invention of polymers that conduct an electrical current—once considered a contradiction in terms—has made possible new substances with many of the advantages of traditional polymers and the added benefit of electrical conductivity. Like most other fields of materials research today, polymer research is turning out products with almost unheard of molecular structures, such as *dendrimers* and *hyperbranched polymers.* These products are so different from any natural or previously manufactured substance that researchers scarcely know the applications in which they may be employed.

CONTENTS

1 The Evolution of Materials

People have long defined civilizations in terms of the materials societies have used to build and make objects. Historians often divide human history into periods such as the Old, Middle, and New Stones Ages; the Bronze Age; the Iron Age; and, much later on in history, the Age of Plastics.

In the earliest stages of human history, people and their hominid ancestors relied on easily obtainable natural materials, such as wood, stone, and clay. They developed techniques for fashioning these materials into the weapons, tools, buildings, and household items needed in their everyday lives. The earliest recorded tools date to 3.1 to 2.5 million years ago from the Hadar region of Africa. These tools were made of volcanic rock and were probably used to shape household items, weapons, and other tools. If the earliest humans made and used tools of organic materials, such as skin or rope, they would all have decayed, and no record of them remains today.

Early Materials

It appears that clay may have been the first material to be treated and reworked by humans so as to produce new properties. This development was possible after the discovery of fire and the development of techniques for its control and use. Once natural clay was formed into some useful shape (such as a pot), it was heated. The new, hard product had applications not possible with the softer natural material. Archaeologists believe that the use of human-made clay products probably dates to the eighth millennium B.C.E.

The use of native metals, such as gold, silver, and copper, goes back even further than the first stone tools. Native metals are elements that occur in the Earth's surface in uncombined form. Examples of decorative objects made of silver, for example, date as early as the eighth millennium B.C.E. in Anatolia, the fifth millennium B.C.E. in parts of North America, and the second millennium B.C.E. in South America. Vedic scripture and other religious writings refer to the use of gold, silver, copper, tin, lead, and iron (although not necessarily in the forms known today) by humans at least three millennia ago.

The first artificial materials were almost certainly fashioned after similar materials found in nature. For example, natural glass is formed when sand is heated to high temperatures, as when it is struck by lightning. One can imagine that early humans witnessed this phenomenon and decided to replicate that process themselves. By the fourth millennium B.C.E., Egyptian artisans had learned how to make glass beads and other objects, although the manufacture of useful objects, such as vases, apparently did not occur until about 1500 B.C.E.

The first significant breakthrough in metallurgy occurred some time after the fourth millennium B.C.E. Metallurgy is the study of metals and the process by which they are extracted from the Earth and converted to useful objects, such as alloys. This event was the discovery of methods for the production of bronze, the first alloy. An alloy is a mixture of two or more elements (at least one of which is a metal) with properties different from those of the elements themselves. Bronze is made from copper and tin in a ratio of at least 9 parts copper to 1 part tin. The temperature required to convert the two elements into the alloy is relatively low (slightly more than the melting point of copper, 1,083°C) and could be attained in ovens available at the time.

Early artisans knew nothing, of course, about the chemical process by which bronze was formed. The first step in that process is usually the conversion of copper and tin oxides to the pure metals. Carbon present in a fire (in the form of charcoal) is the reducing agent in this process:

$$2CuO + C \rightarrow 2Cu + CO_2$$

and

$$2Cu_2O + C \rightarrow 2CO_2 + 4Cu$$

and

$$SnO_2 + C \rightarrow Sn + CO_2$$

The molten copper and tin that result from this process then form a liquid solution that solidifies to form an alloy (bronze) that is stronger and easier to mold than either copper or tin. The advantages of bronze over copper and all other naturally occurring metals soon became obvious, and artisans improved techniques for making the alloy artificially. As the technology for making bronze spread throughout the world, the alloy became the most popular metallic substance for the production of weapons, tools, kitchen implements, and other practical objects. The specific period during which bronze making proliferated differed in various parts of the world, but probably dates to about 3500 B.C.E. at the earliest in some parts of the Middle East. Such techniques did not reach parts of Europe until another 1,500 years later.

The Bronze Age lasted until about 1200 B.C.E., when iron became the new metal of choice for the manufacture of objects. As with bronze, iron was probably produced accidentally in campfires long before it became widely popular. Iron ores occur commonly in nature, and they are reduced at relatively modest temperatures in reactions similar to those for copper and tin. For example:

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$$

and

$$2FeO + C \rightarrow 2Fe + CO_2$$

The iron thus produced does not *appear* to be a useful material, however, since it occurs as spongy material mixed with slag and ash. It is only after these impurities have been removed and the iron has been hammered into a solid mass that it becomes useful for the manufacture of weapons, tools, and other implements. This technology apparently first appeared among the Hittites in about 1500 B.C.E., after which it diffused throughout Anatolia and, eventually, other parts of the world.

Over the next millennium, iron gradually replaced bronze throughout most of the world. One of its great advantages was that iron ores are much more abundant than those of copper and tin, so the manufacture of iron was also much less expensive. Far more people could afford to make or buy tools made of iron than they could tools made of bronze. In addition, iron could be an even stronger, tougher material than bronze, depending on the method by which it was manufactured. Although unknown to people of the time, the form of iron produced by the smelting of iron ores varied greatly depending on the presence of impurities, primarily carbon (from charcoal). Indeed, many centuries later, it was the understanding of how such impurities affect the properties of iron (in forms that we now know of as *steel*) that iron truly became the king of metals during the Industrial Revolution.

By about 500 B.C.E., the discovery and invention of new materials had largely come to an end. The great Greek and Roman civilizations depended almost entirely on materials that had been known and developed in the millennia preceding their appearance, materials such as clay, stone, wood, copper, gold, bronze, and iron. Only one major new innovation occurred during this period, the discovery of hydraulic concrete. Hydraulic concrete was an improvement on a much older building material, lime mortar. Lime mortar is made when limestone (calcium carbonate) is heated to a high temperature, driving off carbon dioxide and leaving behind quicklime (calcium oxide).

$$CaCO_3 \text{ (heated to about 900°C)} \rightarrow CaO + CO_2$$

The quicklime is then mixed with water to form slaked lime (calcium hydroxide).

$$CaO + H_2O \rightarrow Ca(OH)_2$$

As the slaked lime dries, it reacts with carbon dioxide in the air to produce limestone, the raw material from which the final product was made.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

The final product, lime mortar, is an excellent building material and was probably one of the first artificial materials to have been manufactured and used by humans. The Romans, however, discovered a variation of this process that made the final product stronger and longer lasting. They found that the addition of other materials, especially the oxides of aluminum and silicon, greatly enhanced the building properties of the lime mortar. In this improved form, it became known as hydraulic concrete and was used by Roman engineers in many building projects throughout the empire. For example, the Colosseum, Pantheon, Baths of Caracalla, and at least one major aqueduct (the Pont du Gard) were all constructed with hydraulic concrete. The strength of the material is reflected in the fact that even today, 2,000 years after their construction, many of those buildings are still standing and, in some cases, in use.

The Birth of Modern Chemistry and the Discovery of New Materials

With the fall of the Roman Empire and the dawn of the Middle Ages, little or no progress was made in the development of new building materials. Indeed, some technologies were actually lost or virtually forgotten. The use of hydraulic concrete for construction, for example, was rarely used again until the late 18th century, when the technique for its manufacture and use was rediscovered by an English bricklayer named Joseph Aspdin (1788–1855). In 1824, Aspdin applied for a patent for his method for making hydraulic concrete, which later became known as Portland cement. There is little evidence that Aspdin understood the chemistry underlying his method of making cement, but his rediscovery of the product once more made it widely popular as a building material.

By the late 19th century, however, interest in a whole new range of synthetic materials had begun to grow. A strong impetus for this change was the development of a new field of chemistry, organic chemistry. At first, organic chemistry was a relatively limited and not particularly challenging field of chemistry. Organic chemists focused on a study of the chemical compounds contained in plants and animals, in contrast to those found in inorganic, or nonliving, materials. The challenges they assumed were to determine what chemicals were present in living organisms, how much of each was present, the chemical structure of such compounds, and so on. The major difference between organic and inorganic chemistry was that practitioners of the former science made no effort to synthesize the compounds they found in living organisms, only to analyze them.

The reason for this approach to organic chemistry was a dominant philosophy about the nature of organic and inorganic substances. At the time, philosophers and scientists believed that the substances that make up living organisms are, in a very important way, special and different from those that make up inorganic substances, such as rocks and metals. They assumed that organic chemicals contained some special quality, some "breath of life" imparted by a creator god. Given this theory of vitalism, it would have been absurd and even blasphemous for a human chemist to attempt to make organic compounds.

Then, in 1825, the German chemist Friedrich Wöhler (1800–82) made a quite astounding discovery. Upon heating a relatively common inorganic mineral, ammonium cyanate (NH_4CNO), Wöhler found that he was able to produce another compound known as urea [$(NH_2)_2CO$]. The remarkable point about this discovery is that urea is an organic compound, a common excretory product of many animals. As one can see from the formulas of the two compounds, heating of ammonium cyanate apparently causes a rearrangement of the atoms of which it is made, producing urea. Shortly after making his discovery, Wöhler wrote to one of the leading chemists of the day, Jöns Jakob Berzelius (1779–1848), "I must tell you that I can prepare urea without requiring kidneys or an animal, either man or dog." Berzelius wrote back, "It is quite an important and nice discovery