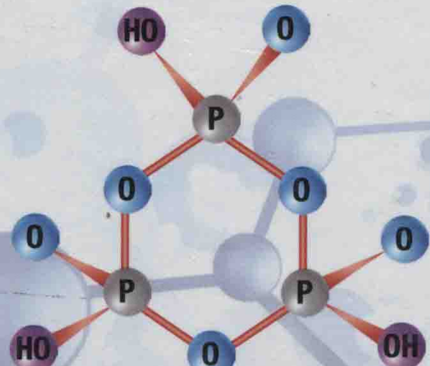
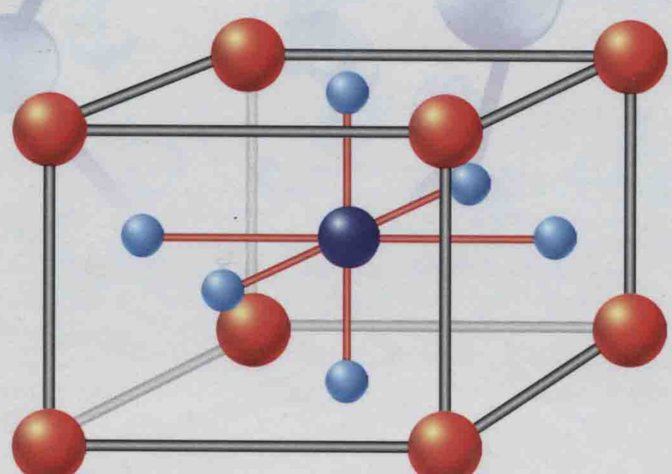
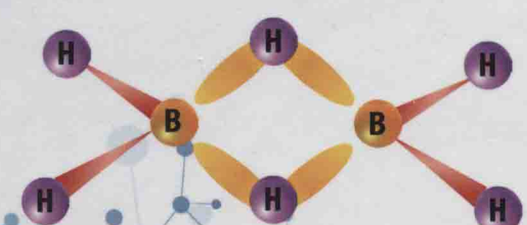
DESCRIPTIVE INORGANIC CHEMISTRY

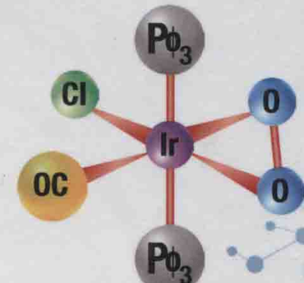
JAMES E. HOUSE AND KATHLEEN A. HOUSE

Third Edition









Descriptive Inorganic Chemistry

Third Edition

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Preface to the Third Edition

The present edition of Descriptive Inorganic Chemistry is based on the objectives that were described in the preface of the second edition. Early chapters provide a tool kit for understanding the structures and reactions that are so important in inorganic chemistry. Of necessity, a brief introduction is provided to the language and approaches of quantum mechanics. In order to provide a more logical separation of topics, Chapter 2 provides essential information on the structure and properties of atoms, and Chapter 3 presents the basic ideas of covalent bonding and symmetry. Following the discussion of structures of solids, emphasis is placed on molecular polarity and the importance of intermolecular interactions, which provide a basis for understanding physical properties of inorganic substances.

In succeeding chapters, the chemistry of elements is presented in an order based on the periodic table. In these chapters, material has been added in numerous places in order to present new information that is relevant and/or timely. Several of the newly presented topics deal with environmental issues. We believe that the result is a more balanced and significant coverage of the field.

In order to show the importance of inorganic chemistry to the entire field of chemistry, we have added Chapter 23, which presents a potpourri of topics that range from uses of iron compounds in treating anemia in oak trees to the use of auranofin, cisplatin, and chloroquine in medicine. The emphasis is placed on the essential factors related to structure and bonding from the standpoint of the inorganic constituents rather on biological functions. The latter are factors best left to courses in biology and biochemistry.

To provide a more appealing book, virtually all illustrations presented in the first two editions have been reconstructed. It must be emphasized that, though we are not graphic artists, we have produced all illustrations. If some of the results look somewhat amateurish, it is because this book is author illustrated rather than professionally illustrated. However, we believe that the illustrations are appropriate and convey the essential information.

It is our opinion that this book meets the objectives of including about as much inorganic chemistry as most students would assimilate in a one-semester course, that the material chosen is appropriate, and that the presentation is lucid and accurate. It is to be hoped that users of this book will agree. Perhaps Dr. Youmans said it best in 1854:

> *Every experienced teacher understands the necessity of making the acquisition of the elementary and foundation principles upon which a science rests, the first business of study. If these are thoroughly mastered, subsequent progress is easy and certain.*
>
> Edward L. Youmans, Chemical Atlas; or the Chemistry of Familiar Objects, D. Appleton & Co., New York, 1854.

April 29, 2015
Bloomington, IL

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Chapter 1

Where It All Comes From

Since the earliest times, man has sought for better materials to use in fabricating objects that were needed. Early man satisfied many requirements by gathering plants for food and fiber, and wood was used for making early tools and shelter. Stone and native metals, especially copper, were also used to make tools and weapons. The ages of man in history are generally identified by the materials that represented the dominant technology employed to fabricate useful objects. The approximate time periods corresponding to these epochs are designated as follows.

? ⟶ Stone Age 4500 BC ⟶ Copper Age 3000 BC ⟶ Bronze Age 1200 BC ⟶ Early Iron Age [illegible] ⟶ Late Iron Age 600 BC

The biblical Old Testament period overlaps with the Copper, Bronze, and Iron Ages, so it is natural that these metals are mentioned frequently in the Bible and in other ancient manuscripts. For example, iron is mentioned about 100 times in the Old Testament, copper 8 times, and bronze more than 150 times. Other metals that were easily obtained (tin and lead) are also described numerous times. In fact, production of metals has been a significant factor in technology and chemistry for many centuries. Processes that are crude by modern standards were used many centuries ago to produce the desired metals and other materials, but the source of raw materials was the same then as it is now. In this chapter, we will present an overview of inorganic chemistry to show its importance in history and to relate it to modern industry.

1.1 THE STRUCTURE OF THE EARTH

There are approximately 16 million known chemical compounds, the vast majority of which are not found in nature. Although many of the known compounds are of little use or importance, some of them would be very difficult or almost impossible to live without. Try to visualize living in a world without concrete, synthetic fibers, fertilizer, steel, soap, glass, or plastics. None of these materials is found in nature in the form in which it is used, and yet they are all produced from naturally occurring raw materials. All of the items listed above and an enormous number of others are created by chemical processes. But created from *what*?

It has been stated that chemistry is the study of matter and its transformations. One of the major objectives of this book is to provide information on how the basic raw materials from the earth are transformed to produce inorganic compounds that are used on an enormous scale. It focuses attention on the transformations of a relatively few inorganic compounds available in nature into many others whether they are at present economically important or not. As you study this book, try to see the connection between obtaining a mineral by mining and the reactions that are used to convert it into end use products. Obviously, this book cannot provide the details for all such processes, but it does attempt to give an overview of inorganic chemistry and its methods and to show its relevance to the production of useful materials. Petroleum and coal are the major raw materials for organic compounds, but the transformation of these materials is not the subject of this book.

As it has been for all time, the earth is the source of all of the raw materials used in the production of chemical substances. The portion of the earth that is accessible for obtaining raw materials is that portion at the surface and slightly above and below the surface. This portion of the earth is referred to in geologic terms as the earth's crust. For thousands of years, man has exploited this region to gather stone, wood, water, and plants. In more modern times, many other chemical raw materials have been taken from the earth and metals have been removed on a huge scale. Although the techniques have changed, we are still limited in access to the resources of the atmosphere, water, and at most, a few miles of depth in the earth. It is the materials found in these regions of the earth that must serve as the starting materials for all of our chemical processes.

Because we are at present limited to the resources of the earth, it is important to understand the main features of its structure. Our knowledge of the structure of the earth has been developed by modern geoscience, and the gross features shown in Figure 1.1 are now generally accepted. The distances shown are approximate, and they vary somewhat from one geographical area to another.

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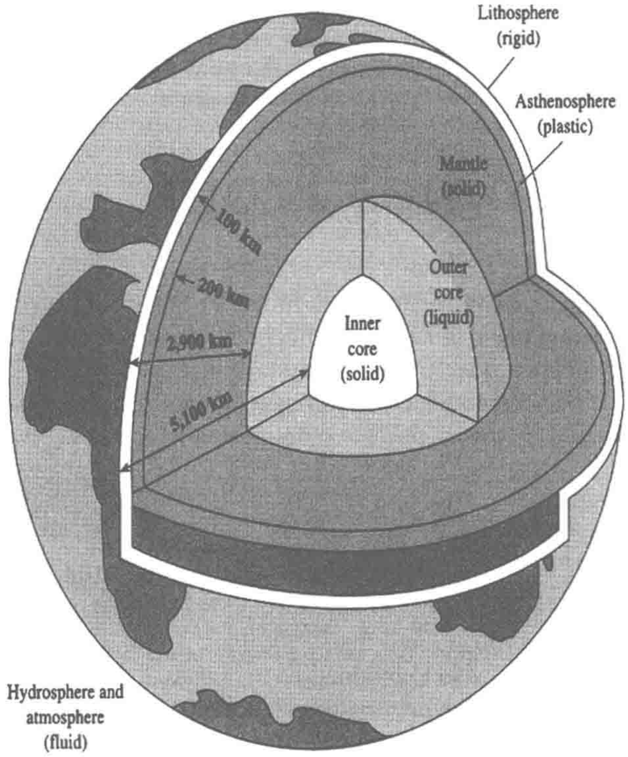

FIGURE 1.1 A cross section of the earth.

The region known as the *upper mantle* extends from the surface of the earth to a depth of approximately 660 km (400 mi). The *lower mantle* extends from a depth of about 660 km to about 3000 km (1800 mi). These layers consist of many substances, including some compounds that contain metals, but rocks composed of silicates are the dominant materials. The upper mantle is sometimes subdivided into the *lithosphere*, extending to a depth of approximately 100 km (60 mi), and the *asthenosphere*, extending from approximately 100 km to about 220 km (140 mi). The solid portion of the earth's crust is regarded as the lithosphere, and the *hydrosphere* and *atmosphere* are the liquid and gaseous regions, respectively. In the asthenosphere, the temperature and pressure are higher than in the lithosphere. As a result, it is generally believed that the asthenosphere is partially molten and softer than the lithosphere lying above it.

The core lies farther below the mantle, and two regions constitute the earth's core. The *outer core* extends from about 3000 km (1800 mi) to about 5000 km (3100 mi), and it consists primarily of molten iron. The *inner core* extends from about 5000 km to the center of the earth about 6500 km (4000 mi) below the surface, and it consists primarily of solid iron. It is generally believed that both core regions contain iron mixed with other metals, but iron is the major component.

The velocity of seismic waves shows unusual behavior in the region between the lower mantle and the outer core. The region where this occurs is at a much higher temperature than is the lower mantle, but it is cooler than the core. Therefore, the region has a large temperature gradient, and its chemistry is believed to be different from that of either the core or mantle. Chemical substances that are likely to be present include metallic oxides such as magnesium oxide and iron oxide, as well as silicon dioxide which is present as a form of *quartz* known as *stishovite* that is stable at high pressure. This is a region of very high pressure with estimates being as high as perhaps a million times that of the atmosphere. Under the conditions of high temperature and pressure, metal oxides react with SiO_2 to form compounds such as $MgSiO_3$ and $FeSiO_3$. Materials that are described by the formula $(Mg,Fe)SiO_3$ (where (Mg,Fe) indicates a material having a composition intermediate between the formulas above) are also produced.

1.2 COMPOSITION OF THE EARTH'S CRUST

Most of the elements shown in the periodic table are found in the earth's crust. A few have been produced artificially, but the rocks, minerals, atmosphere, lakes, and oceans have been the source of the majority of known elements. The abundance by mass of several elements that are major constituents in the earth's crust is shown in Table 1.1.

TABLE 1.1 Abundances of Elements by Mass

Element	O	Si	Al	Fe	Ca	Na	K	Mg	H	All Others
Percent	49.5	25.7	7.5	4.7	3.4	2.6	2.4	1.9	0.9	1.4

Elements such as chlorine, lead, copper, and sulfur occur in very small percentages, and although they are of great importance, they are relatively minor constituents. We must remember that there is a great difference between a material being *present,* and it being *recoverable* in a way that is *economically practical*. For instance, baseball-size nodules rich in manganese, iron, copper, nickel, and cobalt are found in large quantities on the ocean floor at a depth of 5–6 km. In addition, throughout the millennia, gold has been washed out of the earth and transported as minute particles to the oceans. However, it is important to understand that although the oceans are believed to contain vast quantities of metals including billions of tons of gold, there is at present no feasible way to recover these metals. Fortunately, compounds of some of the important elements are found in concentrated form in specific localities, and as a result they are readily accessible. It may be surprising to learn that even coal and petroleum that are used in enormous quantities are relatively minor constituents of the lithosphere. These complex mixtures of organic compounds are present to such a small extent that carbon is not among the most abundant elements. However, petroleum and coal are found concentrated in certain regions so they can be obtained by economically acceptable means. It would be quite different if all the coal and petroleum were distributed uniformly throughout the earth's crust.

1.3 ROCKS AND MINERALS

The chemical resources of early man were limited to the metals and compounds on the earth's surface. A few metals, e.g., copper, silver, and gold, were found uncombined (native) in nature so they have been available for many centuries. It is believed that the iron first used may have been found as uncombined iron that had reached the earth in the form of meteorites. In contrast, elements such as fluorine and sodium are produced by electrochemical reactions, and they have been available a much shorter time.

Most metals are found in the form of naturally occurring chemical compounds called *minerals*. An *ore* is a material that contains a sufficiently high concentration of a mineral to constitute an economically feasible source from which the metal can be recovered. Rocks are composed of solid materials that are found in the earth's crust, and they usually contain mixtures of minerals in varying proportions. Three categories are used to describe rocks based on their origin. Rocks that were formed by the solidification of a molten mass are called *igneous rocks*. Common examples of this type include *granite*, *feldspar*, and *quartz*. *Sedimentary rocks* are those which formed from compacting of small grains that have been deposited as a sediment in a river bed or sea, and they include such common materials as *sandstone*, *limestone*, and *dolomite*. Rocks that have had their composition and structure changed over time by the influences of temperature and pressure are called *metamorphic rocks*. Some common examples are *marble*, *slate*, and *gneiss*.

The lithosphere consists primarily of rocks and minerals. Some of the important classes of metal compounds found in the lithosphere are oxides, sulfides, silicates, phosphates, and carbonates. The atmosphere surrounding the earth contains oxygen so several metals such as iron, aluminum, tin, magnesium, and chromium are found in nature as the oxides. Sulfur is found in many places in the earth's crust (particularly in regions where there is volcanic activity) so some metals are found combined with sulfur as metal sulfides. Metals found as sulfides include copper, silver, nickel, mercury, zinc, and lead. A few metals, especially sodium, potassium, and magnesium, are found as the chlorides. Several carbonates and phosphates occur in the lithosphere, and calcium carbonate and calcium phosphate are particularly important minerals.

1.4 WEATHERING

Conditions on the inside of a rock may be considerably different from those at the surface. Carbon dioxide can be produced by the decay of organic matter, and an acid–base reaction between CO_2 and metal oxides produces metal carbonates. Typical reactions of this type are the following.

$$CaO + CO_2 \rightarrow CaCO_3 \tag{1.1}$$

$$CuO + CO_2 \rightarrow CuCO_3 \tag{1.2}$$

Moreover, because the carbonate ion can react as a base, it can remove H^+ from water to produce hydroxide ions and bicarbonate ions by the following reaction.

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \tag{1.3}$$

Therefore, as an oxide mineral "weathers," reactions of CO_2 and water at the surface lead to the formation of carbonates and bicarbonates. The presence of OH^- can eventually cause part of the mineral to be converted to a metal hydroxide. Because of the basicity of the oxide ion, most metal oxides react with water to produce hydroxides. An important example of such a reaction is

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{1.4}$$

As a result of reactions such as these, a metal oxide may be converted by processes in nature to a metal carbonate or a metal hydroxide. A type of compound closely related to carbonates and hydroxides is known as a basic metal carbonate, and these materials contain both carbonate (CO_3^{2-}) and hydroxide (OH^-) ions. A well-known material of this type is $CuCO_3 \cdot Cu(OH)_2$ or $Cu_2CO_3(OH)_2$ that is the copper-containing mineral known as *malachite*. Another mineral containing copper is *azurite* that has the formula $2\ CuCO_3 \cdot Cu(OH)_2$ or $Cu_3(CO_3)_2(OH)_2$ so it is quite similar to malachite. Azurite and malachite are frequently found together because both are secondary minerals produced by weathering processes. In both cases, the metal oxide, CuO, has been converted to a mixed carbonate/hydroxide compound. This example serves to illustrate how metals are sometimes found in compounds having unusual but closely related formulas. It also shows why ores of metals frequently contain two or more minerals containing the same metal.

Among the most common minerals are the feldspars and clays. These materials have been used for centuries in the manufacture of pottery, china, brick, cement, and other materials. Feldspars include the mineral *orthoclase*, $K_2O \cdot Al_2O_3 \cdot 6\ SiO_2$, but this formula can also be written as $K_2Al_2Si_6O_{16}$. Under the influence of carbon dioxide and water, this mineral weathers by a reaction that can be shown as

$$K_2Al_2Si_6O_{16} + 3\ H_2O + 2\ CO_2 \rightarrow Al_2Si_2O_7 \cdot 2\ H_2O + 2\ KHCO_3 + 4\ SiO_2 \tag{1.5}$$

The product, $Al_2Si_2O_7 \cdot 2\ H_2O$, is known as *kaolinite* and it is one of the aluminosilicates that constitutes clays used in making pottery and china. This example also shows how one mineral can be converted into another by the natural process of weathering.

1.5 OBTAINING METALS

Because of their superior properties, metals have received a great deal of attention since the earliest times. Their immense importance now as well as throughout history indicates that we should describe briefly the processes involved in the production and use of metals. The first metal to be used extensively was copper because of its being found uncombined, but most metals are found combined with other elements in minerals. Minerals are naturally occurring compounds or mixtures of compounds that contain chemical elements. As we have mentioned, a mineral may *contain* some desired metal, but it may not be available in sufficient quantity and purity to serve as a useful *source* of the metal. A commercially usable source of a desired metal is known as an ore.

Most ores are obtained by mining. In some cases, ores are found on or near the surface making it possible for them to be obtained easily. In order to exploit an ore as a useful source of a metal, a large quantity of the ore is usually required. Two of the procedures still used today to obtain ores have been used for centuries. One of these methods is known as *open-pit mining*, and in this technique the ore is recovered by digging in the earth's surface. A second type of mining is *shaft mining* in which a shaft is dug into the earth to gain access to the ore below the surface. Coal and the ores of many metals are obtained by both of these methods. In some parts of the country, huge pits can be seen where the ores of copper and iron have been removed in enormous amounts. In other areas, the evidence of strip mining coal is clearly visible. Of course, the massive effects of shaft mining are much less visible.

Although mechanization makes mining possible on an enormous scale today, mining has been important for millennia. We know from ancient writings such as the Bible that mining and refining of metals have been carried for thousands of years (for example, see Job Chapter 28). Different types of ores are found at different depths, so both open-pit and shaft mining are still in common use. Coal is mined by both open-pit (strip mining) and shaft methods. Copper is mined by the open-pit method in Arizona, Utah, and Nevada, and iron is obtained in this way in Minnesota.

After the metal-bearing ore is obtained, the problem is to obtain the metal from the ore. Frequently, an ore may not have a high enough content of the mineral containing the metal to use it directly. The ore usually contains