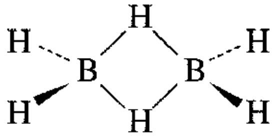
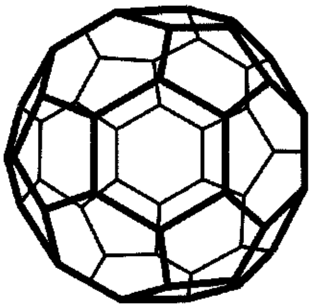




CHAPTER 1

Introduction to Inorganic Chemistry

1-1 WHAT IS INORGANIC CHEMISTRY?

If organic chemistry is defined as the chemistry of hydrocarbon compounds and their derivatives, inorganic chemistry can be described broadly as the chemistry of "everything else." This includes all the remaining elements in the periodic table, as well as carbon, which plays a major role in many inorganic compounds. Organometallic chemistry, a very large and rapidly growing field, bridges both areas by considering compounds containing direct metal-carbon bonds, and includes catalysis of many organic reactions. Bioinorganic chemistry bridges biochemistry and inorganic chemistry, and environmental chemistry includes the study of both inorganic and organic compounds. As can be imagined, the inorganic realm is extremely broad, providing essentially limitless areas for investigation.

1-2 CONTRASTS WITH ORGANIC CHEMISTRY

Some comparisons between organic and inorganic compounds are in order. In both areas, single, double, and triple covalent bonds are found, as shown in Figure 1-1; for inorganic compounds, these include direct metal-metal bonds and metal-carbon bonds. However, although the maximum number of bonds between two carbon atoms is three, there are many compounds containing quadruple bonds between metal atoms. In addition to the sigma and pi bonds common in organic chemistry, quadruply bonded metal atoms contain a delta (δ) bond (Figure 1-2); a combination of one sigma bond, two pi bonds, and one delta bond makes up the quadruple bond. The delta bond is possible in these cases because metal atoms have *d* orbitals to use in bonding, whereas carbon has only *s* and *p* orbitals available.

In organic compounds, hydrogen is nearly always bonded to a single carbon. In inorganic compounds, especially of the Group 13 (IIIA) elements, hydrogen is frequently encountered as a bridging atom between two or more other atoms. Bridging hydrogen atoms can also occur in metal cluster compounds. In these clusters, hydrogen atoms form bridges across edges or faces of polyhedra of metal atoms. Alkyl groups may also act as bridges in inorganic compounds, a function rarely encountered in organic chemistry (except in reaction intermediates). Examples of terminal and bridging hydrogen atoms and alkyl groups in inorganic compounds are shown in Figure 1-3.

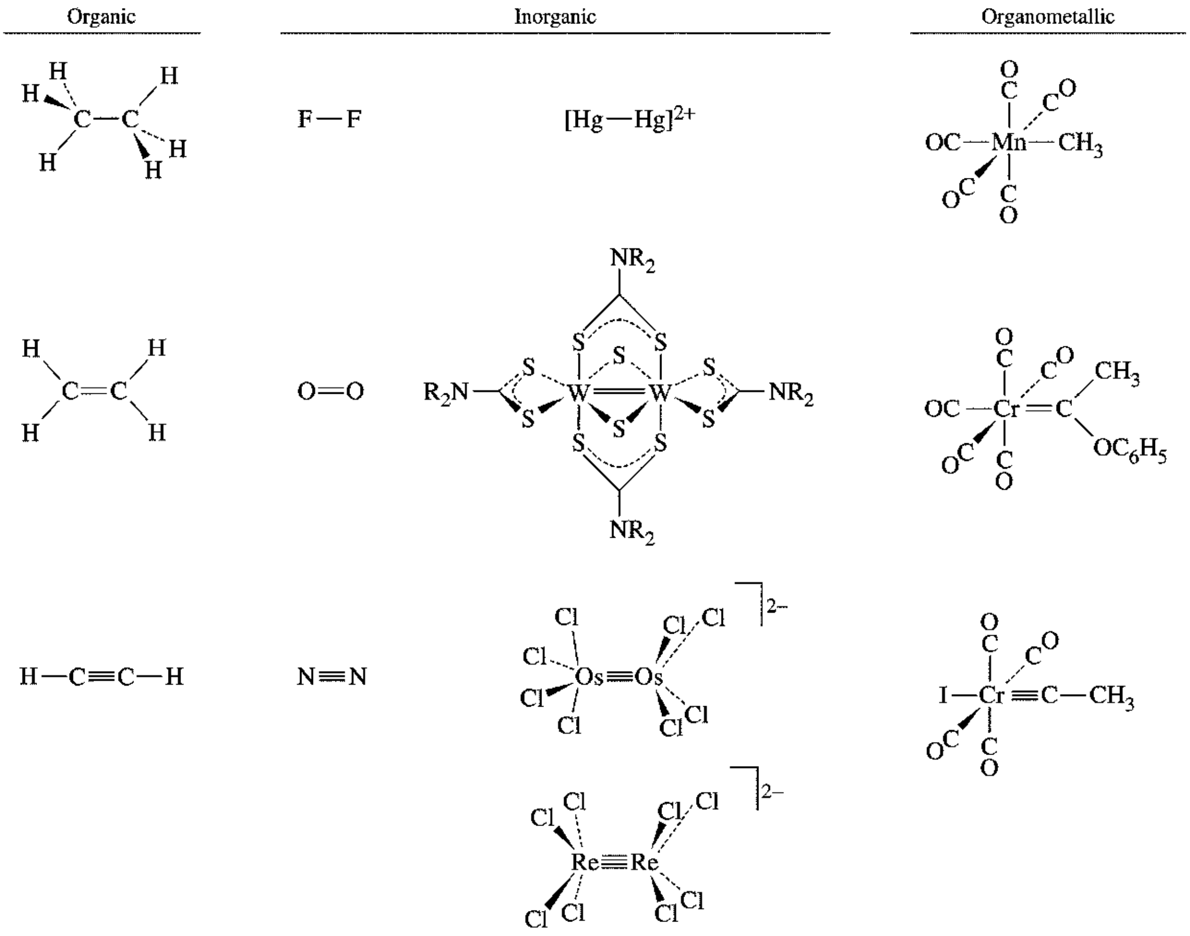


FIGURE 1-1 Single and Multiple Bonds in Organic and Inorganic Molecules.

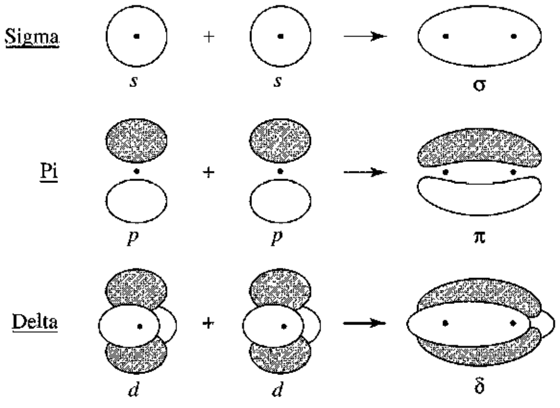
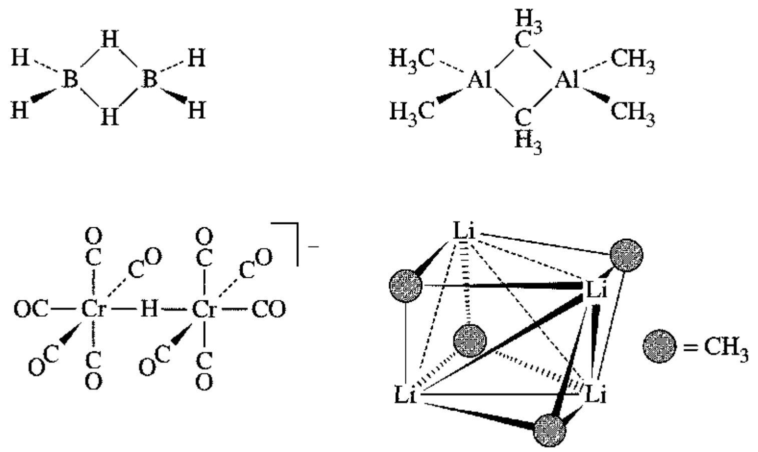


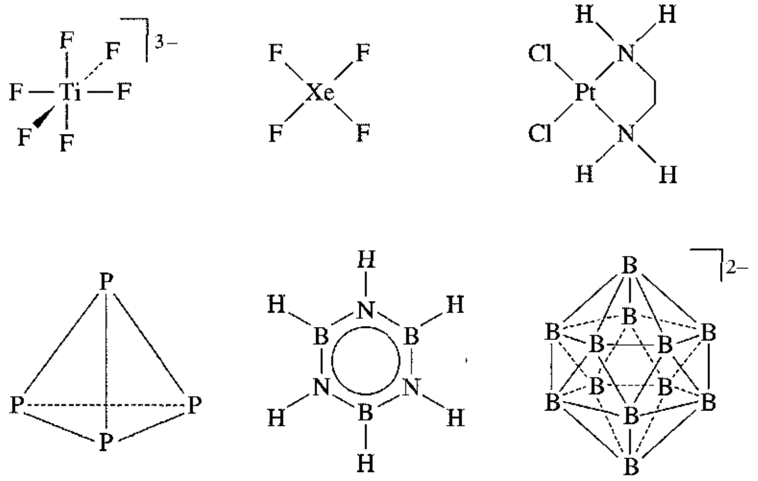
FIGURE 1-2 Examples of Bonding Interactions.

Some of the most striking differences between the chemistry of carbon and that of many other elements are in coordination number and geometry. Although carbon is usually limited to a maximum coordination number of four (a maximum of four atoms bonded to carbon, as in CH_4), inorganic compounds having coordination numbers of five, six, seven, and more are very common; the most common coordination geometry is an octahedral arrangement around a central atom, as shown for $[TiF_6]^{3-}$ in Figure 1-4.



Each CH_3 bridges a face of the Li_4 tetrahedron

FIGURE 1-3 Examples of Inorganic Compounds Containing Terminal and Bridging Hydrogens and Alkyl Groups.



$B_{12}H_{12}^{2-}$ (not shown: one hydrogen on each boron)

FIGURE 1-4 Examples of Geometries of Inorganic Compounds.

Furthermore, inorganic compounds present coordination geometries different from those found for carbon. For example, although 4-coordinate carbon is nearly always tetrahedral, both tetrahedral and square planar shapes occur for 4-coordinate compounds of both metals and nonmetals. When metals are the central atoms, with anions or neutral molecules bonded to them (frequently through N, O, or S), these are called coordination complexes; when carbon is the element directly bonded to metal atoms or ions, they are called organometallic compounds.

The tetrahedral geometry usually found in 4-coordinate compounds of carbon also occurs in a different form in some inorganic molecules. Methane contains four hydrogens in a regular tetrahedron around carbon. Elemental phosphorus is tetratomic (P_4) and also is tetrahedral, but with no central atom. Examples of some of the geometries found for inorganic compounds are shown in Figure 1-4.

Aromatic rings are common in organic chemistry, and aryl groups can also form sigma bonds to metals. However, aromatic rings can also bond to metals in a dramatically different fashion using their pi orbitals, as shown in Figure 1-5. The result is a metal atom bonded above the center of the ring, almost as if suspended in space. In

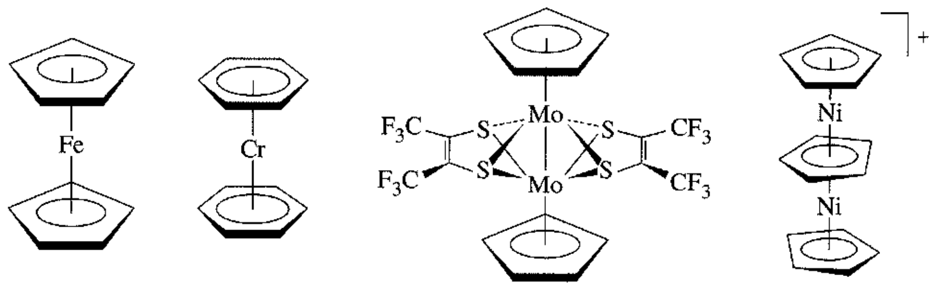


FIGURE 1-5 Inorganic Compounds Containing Pi-bonded Aromatic Rings.

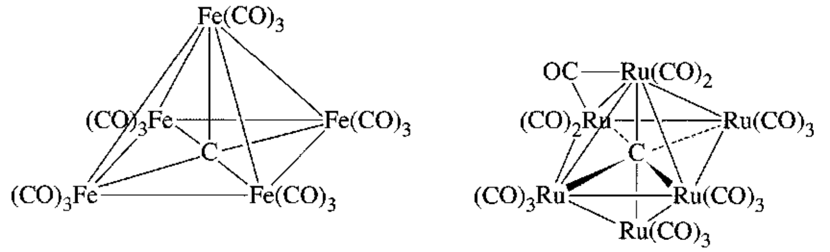


FIGURE 1-6 Carbon-centered Metal Clusters.

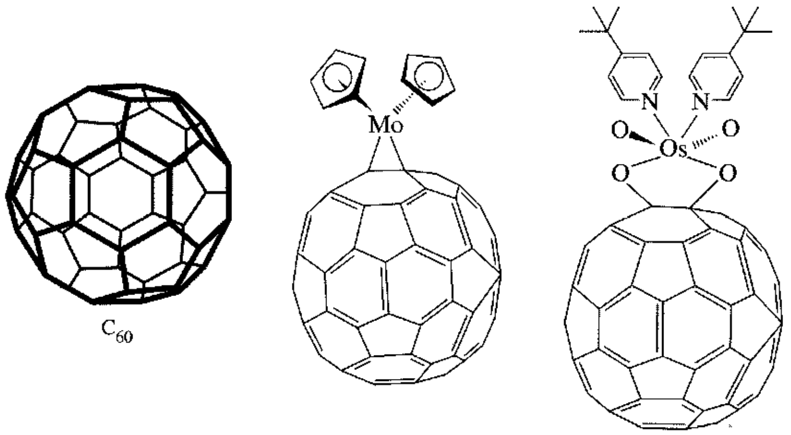


FIGURE 1-7 Fullerene Compounds.

many cases, metal atoms are sandwiched between two aromatic rings. Multiple-decker sandwiches of metals and aromatic rings are also known.

Carbon plays an unusual role in a number of metal cluster compounds in which a carbon atom is at the center of a polyhedron of metal atoms. Examples of carbon-centered clusters of five, six, or more metals are known; two of these are shown in Figure 1-6. The contrast of the role that carbon plays in these clusters to its usual role in organic compounds is striking, and attempting to explain how carbon can form bonds to the surrounding metal atoms in clusters has provided an interesting challenge to theoretical inorganic chemists. A molecular orbital picture of bonding in these clusters is discussed in Chapter 15.

In addition, during the past decade, the realm of a new class of carbon clusters, the fullerenes, has flourished. The most common of these clusters, C_{60}, has been labeled "buckminsterfullerene" after the developer of the geodesic dome and has served as the core of a variety of derivatives (Figure 1-7).

There are no sharp dividing lines between subfields in chemistry. Many of the subjects in this book, such as acid-base chemistry and organometallic reactions, are of vital interest to organic chemists. Others, such as oxidation-reduction reactions, spectra, and solubility relations, also interest analytical chemists. Subjects related to structure determination, spectra, and theories of bonding appeal to physical chemists. Finally, the use of organometallic catalysts provides a connection to petroleum and polymer chemistry, and the presence of coordination compounds such as hemoglobin and metal-containing enzymes provides a similar tie to biochemistry. This list is not intended to describe a fragmented field of study, but rather to show some of the interconnections between inorganic chemistry and other fields of chemistry.

The remainder of this chapter is devoted to the origins of inorganic chemistry, from the creation of the elements to the present. It is a short history, intended only to provide the reader with a sense of connection to the past and with a means of putting some of the topics of inorganic chemistry into the context of larger historical events. In many later chapters, a brief history of each topic is given, with the same intention. Although time and space do not allow for much attention to history, we want to avoid the impression that any part of chemistry has sprung full-blown from any one person's work or has appeared suddenly. Although certain events, such as a new theory or a new type of compound or reaction, can later be identified as marking a dramatic change of direction in inorganic chemistry, all new ideas are built on past achievements. In some cases, experimental observations from the past become understandable in the light of new theoretical developments. In others, the theory is already in place, ready for the new compounds or phenomena that it will explain.

1-3

GENESIS OF THE ELEMENTS (THE BIG BANG) AND FORMATION OF THE EARTH

We begin our study of inorganic chemistry with the genesis of the elements and the creation of the universe. Among the difficult tasks facing anyone who attempts to explain the origin of the universe are the inevitable questions: "What about the time just before the creation? Where did the starting material, whether energy or matter, come from?" The whole idea of an origin at a specific time means that there was nothing before that instant. By its very nature, no theory attempting to explain the origin of the universe can be expected to extend infinitely far back in time.

Current opinion favors the big bang theory[1] over other creation theories, although many controversial points are yet to be explained. Other theories, such as the steady-state or oscillating theories, have their advocates, and the creation of the universe is certain to remain a source of controversy and study.

According to the big bang theory, the universe began about 1.8×10^{10} years ago with an extreme concentration of energy in a very small space. In fact, extrapolation back to the time of origin requires zero volume and infinite temperature. Whether this is true or not is still a source of argument. What is almost universally agreed on is that the universe is expanding rapidly, from an initial event during which neutrons were formed and decayed quickly (half-life = 11.3 min) into protons, electrons, and antineutrinos:

$$\mathrm{n} \longrightarrow \mathrm{p} + \mathrm{e}^- + \bar{\nu}_\mathrm{e}$$

or

$$^{1}_{0}\mathrm{n} \longrightarrow {}^{1}_{1}\mathrm{H} + {}^{\;\,0}_{-1}\mathrm{e} + \bar{\nu}_\mathrm{e}$$

In this and subsequent equations,

$^{1}_{1}\mathrm{H} = \mathrm{p} =$ a proton of charge +1 and mass 1.007 atomic mass unit (amu)[2]

$\gamma =$ a gamma ray (high-energy photon) with zero mass

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[1] P. A. Cox, *The Elements, Their Origin, Abundance and Distribution*, Oxford University Press, Oxford, 1990, pp. 66–92; J. Selbin, *J. Chem. Educ.*, **1973**, *50*, 306, 380; A. A. Penzias, *Science*, **1979**, *105*, 549.

[2] More accurate masses are given inside the back cover of this text.

${}_{-1}^{0}e = e^- =$ an electron of charge -1 and mass $\frac{1}{1823}$ amu (also known as a β particle)

${}_{1}^{0}e = e^+ =$ a positron with charge $+1$ and mass $\frac{1}{1823}$ amu

ν_e = a neutrino with no charge and a very small mass

$\bar{\nu}_e$ = an antineutrino with no charge and a very small mass

${}_{0}^{1}n$ = a neutron with no charge and a mass of 1.009 amu

Nuclei are described by the convention

$${}_{\text{atomic number}}^{\text{mass number}}\text{symbol} \quad \text{or} \quad {}_{\text{nuclear charge}}^{\text{proton plus neutrons}}\text{symbol}$$

After about 1 second, the universe was made up of a plasma of protons, neutrons, electrons, neutrinos, and photons, but the temperature was too high to allow the formation of atoms. This plasma and the extremely high energy caused fast nuclear reactions. As the temperature dropped to about 10^9 K, the following reactions occurred within a matter of minutes:

$$\begin{aligned} {}_{1}^{1}H + {}_{0}^{1}n &\longrightarrow {}_{1}^{2}H + \gamma \\ {}_{1}^{2}H + {}_{1}^{2}H &\longrightarrow {}_{1}^{3}H + {}_{1}^{1}H \\ {}_{1}^{2}H + {}_{1}^{2}H &\longrightarrow {}_{2}^{3}He + {}_{0}^{1}n \\ {}_{2}^{3}He + {}_{0}^{1}n &\longrightarrow {}_{2}^{4}He + \gamma \end{aligned}$$

The first is the limiting reaction because the reverse reaction is also fast. The interplay of the rates of these reactions gives an atomic ratio of He/H $= 1/10$, which is the abundance observed in young stars.

By this time, the temperature had dropped enough to allow the positive particles to capture electrons to form atoms. Because atoms interact less strongly with electromagnetic radiation than do the individual subatomic particles, the atoms could now interact with each other more or less independently from the radiation. The atoms began to condense into stars, and the radiation moved with the expanding universe. This expansion caused a red shift, leaving the background radiation with wavelengths in the millimeter range, which is characteristic of a temperature of 2.7 K. This radiation was observed in 1965 by Penzias and Wilson and is supporting evidence for the big bang theory.

Within one half-life of the neutron (11.3 min), half the matter of the universe consisted of protons and the temperature was near 5×10^8 K. The nuclei formed in the first 30 to 60 minutes were those of deuterium (^{2}H), ^{3}He, ^{4}He, and ^{5}He. (Helium 5 has a very short half-life of 2×10^{-21} seconds and decays back to helium 4, effectively limiting the mass number of the nuclei formed by these reactions to 4.) The following reactions show how these nuclei can be formed in a process called *hydrogen burning*:

$$\begin{aligned} {}_{1}^{1}H + {}_{1}^{1}H &\longrightarrow {}_{1}^{2}H + {}_{1}^{0}e + \nu_e \\ {}_{1}^{2}H + {}_{1}^{1}H &\longrightarrow {}_{2}^{3}He + \gamma \\ {}_{2}^{3}He + {}_{2}^{3}He &\longrightarrow {}_{2}^{4}He + 2\,{}_{1}^{1}H \end{aligned}$$

The expanding material from these first reactions began to gather together into galactic clusters and then into more dense stars, where the pressure of gravity kept the temperature high and promoted further reactions. The combination of hydrogen and helium with many protons and neutrons led rapidly to the formation of heavier elements. In stars with internal temperatures of 10^7 to 10^8 K, the reactions forming ${}^{2}\text{H}$, ${}^{3}\text{He}$, and ${}^{4}\text{He}$ continued, along with reactions that produced heavier nuclei. The following *helium-burning* reactions are among those known to take place under these conditions:

$$\begin{aligned}
2\,{}^{4}_{2}\text{He} &\longrightarrow {}^{8}_{4}\text{Be} + \gamma \\
{}^{4}_{2}\text{He} + {}^{8}_{4}\text{Be} &\longrightarrow {}^{12}_{6}\text{C} + \gamma \\
{}^{12}_{6}\text{C} + {}^{1}_{1}\text{H} \longrightarrow {}^{13}_{7}\text{N} &\longrightarrow {}^{13}_{6}\text{C} + {}^{0}_{1}\text{e} + \nu_e
\end{aligned}$$

In more massive stars (temperatures of 6 × 10^8 K or higher), the carbon-nitrogen cycle is possible:

$$\begin{aligned}
{}^{12}_{6}\text{C} + {}^{1}_{1}\text{H} &\longrightarrow {}^{13}_{7}\text{N} + \gamma \\
{}^{13}_{7}\text{N} &\longrightarrow {}^{13}_{6}\text{C} + {}^{0}_{1}\text{e} + \nu_e \\
{}^{13}_{6}\text{C} + {}^{1}_{1}\text{H} &\longrightarrow {}^{14}_{7}\text{N} + \gamma \\
{}^{14}_{7}\text{N} + {}^{1}_{1}\text{H} &\longrightarrow {}^{15}_{8}\text{O} + \gamma \\
{}^{15}_{8}\text{O} &\longrightarrow {}^{15}_{7}\text{N} + {}^{0}_{1}\text{e} + \nu_e \\
{}^{15}_{7}\text{N} + {}^{1}_{1}\text{H} &\longrightarrow {}^{4}_{2}\text{He} + {}^{12}_{6}\text{C}
\end{aligned}$$

The net result of this cycle is the formation of helium from hydrogen, with gamma rays, positrons, and neutrinos as byproducts. In addition, even heavier elements are formed:

$$\begin{aligned}
{}^{12}_{6}\text{C} + {}^{12}_{6}\text{C} &\longrightarrow {}^{20}_{10}\text{Ne} + {}^{4}_{2}\text{He} \\
2\,{}^{16}_{8}\text{O} &\longrightarrow {}^{28}_{14}\text{Si} + {}^{4}_{2}\text{He} \\
2\,{}^{16}_{8}\text{O} &\longrightarrow {}^{31}_{16}\text{S} + {}^{1}_{0}\text{n}
\end{aligned}$$

At still higher temperatures, further reactions take place:

$$\begin{aligned}
\gamma + {}^{28}_{14}\text{Si} &\longrightarrow {}^{24}_{12}\text{Mg} + {}^{4}_{2}\text{He} \\
{}^{28}_{14}\text{Si} + {}^{4}_{2}\text{He} &\longrightarrow {}^{32}_{16}\text{S} + \gamma \\
{}^{32}_{16}\text{S} + {}^{4}_{2}\text{He} &\longrightarrow {}^{36}_{18}\text{Ar} + \gamma
\end{aligned}$$

Even heavier elements can be formed, with the actual amounts depending on a complex relationship among their inherent stability, the temperature of the star, and the lifetime of the star. The curve of inherent stability of nuclei has a maximum at ${}^{56}_{26}\text{Fe}$, accounting for the high relative abundance of iron in the universe. If these reactions continued indefinitely, the result should be nearly complete dominance of elements near iron over the other elements. However, as parts of the universe cooled, the reactions slowed or stopped. Consequently, both lighter and heavier elements are common. Formation of elements of higher atomic number takes place by the addition of neutrons to a nucleus, followed by electron emission decay. In environments of low neutron density, this addition of neutrons is relatively slow, one neutron at a time; in the high neutron density environment of a nova, 10 to 15 neutrons may be added in a very short time, and the resulting nucleus is then neutron rich:

$$ {}^{56}_{26}\text{Fe} + 13\,{}^{1}_{0}\text{n} \longrightarrow {}^{69}_{26}\text{Fe} \longrightarrow {}^{69}_{27}\text{Co} + {}^{0}_{-1}\text{e} $$

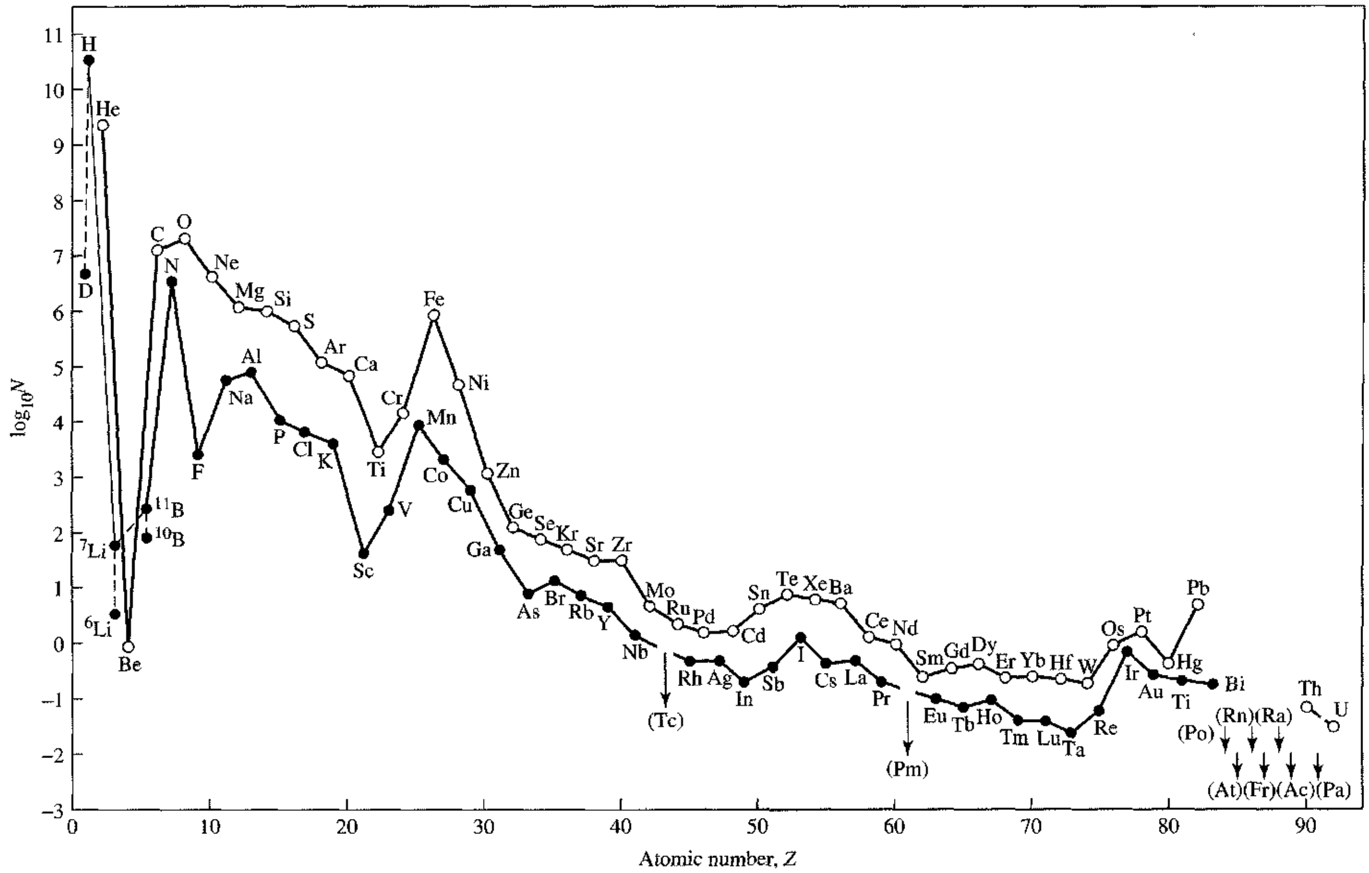

FIGURE 1-8 Cosmic Abundances of the Elements. (Reprinted with permission from N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Butterworth-Heinemann, Oxford, 1997, p. 4.)

The very heavy elements are also formed by reactions such as this. After the addition of the neutrons, β decay (loss of electrons from the nucleus as a neutron is converted to a proton plus an electron) leads to nuclei with larger atomic numbers. Figure 1-8 shows the cosmic abundances of some of the elements.

Gravitational attraction combined with rotation gradually formed the expanding cloud of material into relatively flat spiral galaxies containing millions of stars each. Complex interactions within the stars led to black holes and other types of stars, some of which exploded as supernovas and scattered their material widely. Further gradual accretion of some of this material into planets followed. At the lower temperatures found in planets, the buildup of heavy elements stopped, and decay of unstable radioactive isotopes of the elements became the predominant nuclear reactions.

1-4

NUCLEAR REACTIONS AND RADIOACTIVITY

Some nuclei were formed that were stable, never undergoing further reactions. Others have lifetimes ranging from 10^{16} years to 10^{-16} second. The usual method of describing nuclear decay is in terms of the **half-life**, or the time needed for half the nuclei to react. Because decay follows first-order kinetics, the half-life is a well-defined value, not dependent on the amount present. In addition to the overall curve of nuclear stability, which has its most stable region near atomic number $Z = 26$, combinations of protons and neutrons at each atomic number exhibit different stabilities. In some elements such as fluorine (^{19}F), there is only one stable **isotope** (a specific combination of protons and neutrons). In others, such as chlorine, there are two or more stable isotopes. ^{35}Cl has a natural abundance of 75.77%, and ^{37}Cl has a natural abundance of 24.23%. Both are stable, as are all the natural isotopes of the lighter elements. The radioactive isotopes of these elements have short half-lives and have had more than enough time to decay to more stable elements. ^{3}H, ^{14}C, and a few other radioactive nuclei are continually being formed by cosmic rays and have a low constant concentration.

Heavier elements ($Z = 40$ or higher) may also have radioactive isotopes with longer half-lives. As a result, some of these radioactive isotopes have not had time to decay completely, and the natural substances are radioactive. Further discussion of isotopic abundances and radioactivity can be found in larger or more specialized sources.[3]

As atomic mass increases, the ratio of neutrons to protons in stable isotopes gradually increases from 1 : 1 to 1.6 : 1 for $^{238}_{92}U$. There is also a set of nuclear energy levels similar to the electron energy levels described in Chapter 2 that result in stable nuclei with 2, 8, 20, 28, 50, 82, and 126 protons or neutrons. In nature, the most stable nuclei are those with the numbers of both protons and neutrons matching one of these numbers; $^{4}_{2}He$, $^{16}_{8}O$, $^{40}_{20}Ca$, and $^{208}_{82}Pb$ are examples.

Elements not present in nature can be formed by bombardment of one element with nuclei of another; if the atoms are carefully chosen and the energy is right, the two nuclei can merge to form one nucleus and then eject a portion of the nucleus to form a new element. This procedure has been used to extend the periodic table beyond uranium. Neptunium and plutonium can be formed by addition of neutrons to uranium followed by release of electrons (β particles). Still heavier elements require heavier projectiles and higher energies. Using this approach, elements up to 112, temporarily called ununbium for its atomic number, have been synthesized. Synthesis of elements 114, 116, and 118 has been claimed, but the claim for 118 was later withdrawn. Calculations indicate that there may be some relatively stable (half-lives longer than a few seconds) isotopes of some of the superheavy elements, if the appropriate target isotopes and projectiles are used. Suggestions include ^{248}Cm, ^{250}Cm, and ^{244}Pu as targets and ^{48}Ca as the projectile. Predictions such as this have fueled the search for still heavier elements, even though their stability is so low that they must be detected within seconds of their creation before they decompose to lighter elements. Hoffman and Lee[4] have reviewed the efforts to study the chemistry of these new elements. The subtitle of their article, "One Atom at a Time," described the difficulty of such studies. In one case, α-daughter decay chains of ^{265}Sg were detected from only three atoms during 5000 experiments, but this was sufficient to show that Sg(VI) is similar to W(VI) and Mo(VI) in forming neutral or negative species in HNO_3-HF solution, but not like U(VI), which forms $[UO_2]^{2+}$ under these conditions. Element 108, hassium, formed by bombarding ^{248}Cm with high-energy atoms of ^{26}Mg, was found to form an oxide similar to that of osmium on the basis of six oxide molecules carried from the reaction site to a detector by a stream of helium.[5] This may be the most massive atom on which "chemistry" has been performed to date.

1-5 DISTRIBUTION OF ELEMENTS ON EARTH

Theories that attempt to explain the formation of the specific structures of the Earth are at least as numerous as those for the formation of the universe. Although the details of these theories differ, there is general agreement that the Earth was much hotter during its early life, and that the materials fractionated into gaseous, liquid, and solid states at that time. As the surface of the Earth cooled, the lighter materials in the crust solidified and still float on a molten inner layer, according to the plate tectonics

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[3] N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, Oxford, 1997; J. Silk, *The Big Bang. The Creation and Evolution of the Universe*, W. H. Freeman, San Francisco, 1980.

[4] D. C. Hoffman and D. M. Lee, *J. Chem. Educ.*, **1999**, *76*, 331.

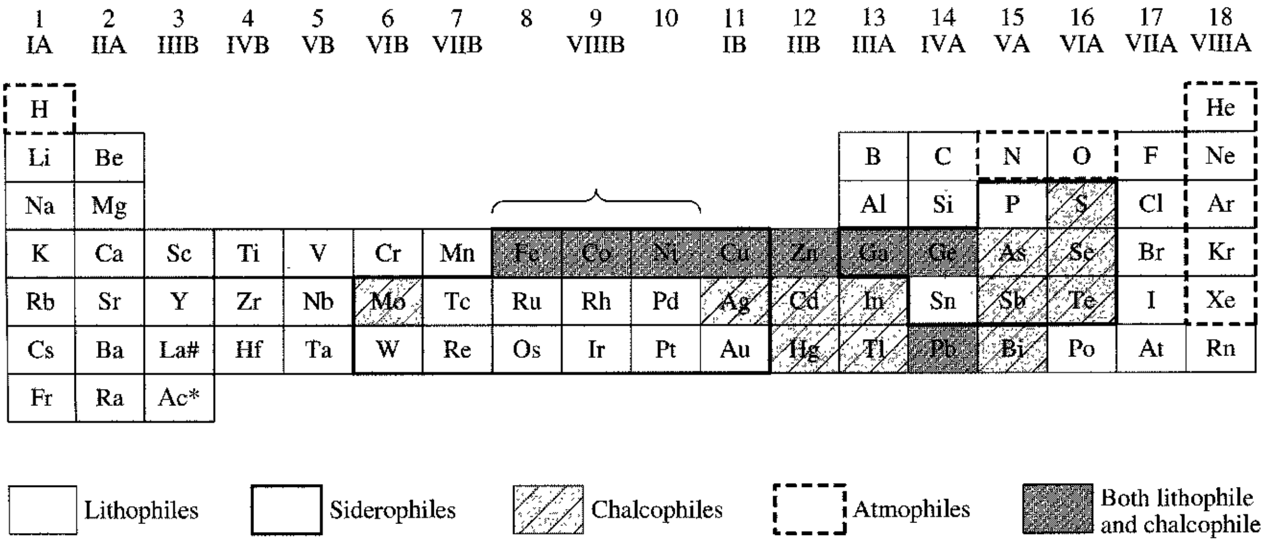
[5] *Chem. Eng. News*, June 4, 2001, p. 47.

explanation of geology. There is also general agreement that the Earth has a core of iron and nickel, which is solid at the center and liquid above that. The outer half of the Earth's radius is composed of silicate minerals in the mantle; silicate, oxide, and sulfide minerals in the crust; and a wide variety of materials at the surface, including abundant water and the gases of the atmosphere.

The different types of forces apparent in the early planet Earth can now be seen indirectly in the distribution of minerals and elements. In locations where liquid magma broke through the crust, compounds that are readily soluble in such molten rock were carried along and deposited as ores. Fractionation of the minerals then depended on their melting points and solubilities in the magma. In other locations, water was the source of the formation of ore bodies. At these sites, water leached minerals from the surrounding area and later evaporated, leaving the minerals behind. The solubilities of the minerals in either magma or water depend on the elements, their oxidation states, and the other elements with which they are combined. A rough division of the elements can be made according to their ease of reduction to the element and their combination with oxygen and sulfur. **Siderophiles** (iron-loving elements) concentrate in the metallic core, **lithophiles** (rock-loving elements) combine primarily with oxygen and the halides and are more abundant in the crust, and **chalcophiles** (Greek, *Khalkos*, copper) combine more readily with sulfur, selenium, and arsenic and are also found in the crust. **Atmophiles** are present as gases. These divisions are shown in the periodic table in Figure 1-9.

As an example of the action of water, we can explain the formation of bauxite (hydrated Al_2O_3) deposits by the leaching away of the more soluble salts from aluminosilicate deposits. The silicate portion is soluble enough in water that it can be leached away, leaving a higher concentration of aluminum. This is shown in the reaction

$$\underset{\text{aluminosilicate}}{4\,KAlSi_3O_8(s)} + 4\,CO_2 + 22\,H_2O \longrightarrow 4\,K^+ + 4\,HCO_3^- + \underset{\substack{\text{higher concentration}\\ \text{of Al}}}{Al_4Si_4O_{10}(OH)_8(s)} + \underset{\substack{\text{silicate}\\ \text{(leached away)}}}{8\,H_4SiO_4(aq)}$$



\# Including lanthanides Ce through Lu
* Including actinides Th, U

FIGURE 1-9 Geochemical Classification of the Elements. (Adapted with permission from P. A. Cox, *The Elements, Their Origin, Abundance, and Distribution*, Oxford University Press, Oxford, 1990, p. 13.)

in which H_4SiO_4 is a generic representation for a number of soluble silicate species. This mechanism provides at least a partial explanation for the presence of bauxite deposits in tropical areas or in areas that once were tropical, with large amounts of rainfall in the past.

Further explanations of these geological processes must be left to more specialized sources.[6] Such explanations are based on concepts treated later in this text. For example, modern acid-base theory helps explain the different solubilities of minerals in water or molten rock and their resulting deposits in specific locations. The divisions illustrated in Figure 1-9 can be partly explained by this theory, which is discussed in Chapter 6 and used in later chapters.

1-6

THE HISTORY OF INORGANIC CHEMISTRY

Even before alchemy became a subject of study, many chemical reactions were used and the products applied to daily life. For example, the first metals used were probably gold and copper, which can be found in the metallic state. Copper can also be readily formed by the reduction of malachite—basic copper carbonate, $Cu_2(CO_3)(OH)_2$—in charcoal fires. Silver, tin, antimony, and lead were also known as early as 3000 BC. Iron appeared in classical Greece and in other areas around the Mediterranean Sea by 1500 BC. At about the same time, colored glasses and ceramic glazes, largely composed of silicon dioxide (SiO_2, the major component of sand) and other metallic oxides, which had been melted and allowed to cool to amorphous solids, were introduced.

Alchemists were active in China, Egypt, and other centers of civilization early in the first centuries AD. Although much effort went into attempts to "transmute" base metals into gold, the treatises of these alchemists also described many other chemical reactions and operations. Distillation, sublimation, crystallization, and other techniques were developed and used in their studies. Because of the political and social changes of the time, alchemy shifted into the Arab world and later (about 1000 to 1500 AD) reappeared in Europe. Gunpowder was used in Chinese fireworks as early as 1150, and alchemy was also widespread in China and India at that time. Alchemists appeared in art, literature, and science until at least 1600, by which time chemistry was beginning to take shape as a science. Roger Bacon (1214–1294), recognized as one of the first great experimental scientists, also wrote extensively about alchemy.

By the 17th century, the common strong acids (nitric, sulfuric, and hydrochloric) were known, and more systematic descriptions of common salts and their reactions were being accumulated. The combination of acids and bases to form salts was appreciated by some chemists. As experimental techniques improved, the quantitative study of chemical reactions and the properties of gases became more common, atomic and molecular weights were determined more accurately, and the groundwork was laid for what later became the periodic table. By 1869, the concepts of atoms and molecules were well established, and it was possible for Mendeleev and Meyer to describe different forms of the periodic table. Figure 1-10 illustrates Mendeleev's original periodic table.

The chemical industry, which had been in existence since very early times in the form of factories for the purification of salts and the smelting and refining of metals, expanded as methods for the preparation of relatively pure materials became more common. In 1896, Becquerel discovered radioactivity, and another area of study was opened. Studies of subatomic particles, spectra, and electricity finally led to the atomic theory of Bohr in 1913, which was soon modified by the quantum mechanics of Schrödinger and Heisenberg in 1926 and 1927.

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[6] J. E. Fergusson, *Inorganic Chemistry and the Earth*, Pergamon Press, Elmsford, NY, 1982; J. E. Fergusson, *The Heavy Elements*, Pergamon Press, Elmsford, NY, 1990.

			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	Ta = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 53	Rh = 104.4	Pt = 197.4
			Fe = 56	Ru = 104.2	Ir = 198
			Ni = Co = 59	Pd = 106.6	Os = 199
H = 1			Cu = 63.4	Ag = 108	Hg = 200
	Be = 9.4	Mg = 24	Zn = 65.2	Cd = 112	
	B = 11	Al = 27.4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
	O = 16	S = 32	Se = 79.4	Te = 128?	
	F = 19	Cl = 35.5	Br = 80	J = 127	
Li = 7	Na = 23	K = 39	Rb = 85.4	Cs = 133	Tl = 204
		Ca = 40	Sr = 87.6	Ba = 137	Pb = 207
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75.6	Th = 118 ?		

FIGURE 1-10 Mendeleev's 1869 Periodic Table. Two years later, he revised his table into a form similar to a modern short-form periodic table, with eight groups across.

Inorganic chemistry as a field of study was extremely important during the early years of the exploration and development of mineral resources. Qualitative analysis methods were developed to help identify minerals and, combined with quantitative methods, to assess their purity and value. As the industrial revolution progressed, so did the chemical industry. By the early 20th century, plants for the production of ammonia, nitric acid, sulfuric acid, sodium hydroxide, and many other inorganic chemicals produced on a large scale were common.

In spite of the work of Werner and Jørgensen on coordination chemistry near the beginning of the 20th century and the discovery of a number of organometallic compounds, the popularity of inorganic chemistry as a field of study gradually declined during most of the first half of the century. The need for inorganic chemists to work on military projects during World War II rejuvenated interest in the field. As work was done on many projects (not least of which was the Manhattan Project, in which scientists developed the fission bomb that later led to the development of the fusion bomb), new areas of research appeared, old areas were found to have missing information, and new theories were proposed that prompted further experimental work. A great expansion of inorganic chemistry started in the 1940s, sparked by the enthusiasm and ideas generated during World War II.

In the 1950s, an earlier method used to describe the spectra of metal ions surrounded by negatively charged ions in crystals (**crystal field theory**)[7] was extended by the use of molecular orbital theory[8] to develop **ligand field theory** for use in coordination compounds, in which metal ions are surrounded by ions or molecules that donate electron pairs. This theory, explained in Chapter 10, gave a more complete picture of the bonding in these compounds. The field developed rapidly as a result of this theoretical framework, the new instruments developed about this same time, and the generally reawakened interest in inorganic chemistry.

In 1955, Ziegler[9] and associates and Natta[10] discovered organometallic compounds that could catalyze the polymerization of ethylene at lower temperatures and

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[7] H. A. Bethe, *Ann. Physik*, **1929**, *3*, 133.

[8] J. S. Griffith and L. E. Orgel, *Q. Rev. Chem. Soc.*, **1957**, *XI*, 381.

[9] K. Ziegler, E. Holzkamp, H. Breil, and H. Martin, *Angew. Chem.*, **1955**, *67*, 541.

[10] G. Natta, *J. Polym. Sci.*, **1955**, *16*, 143.

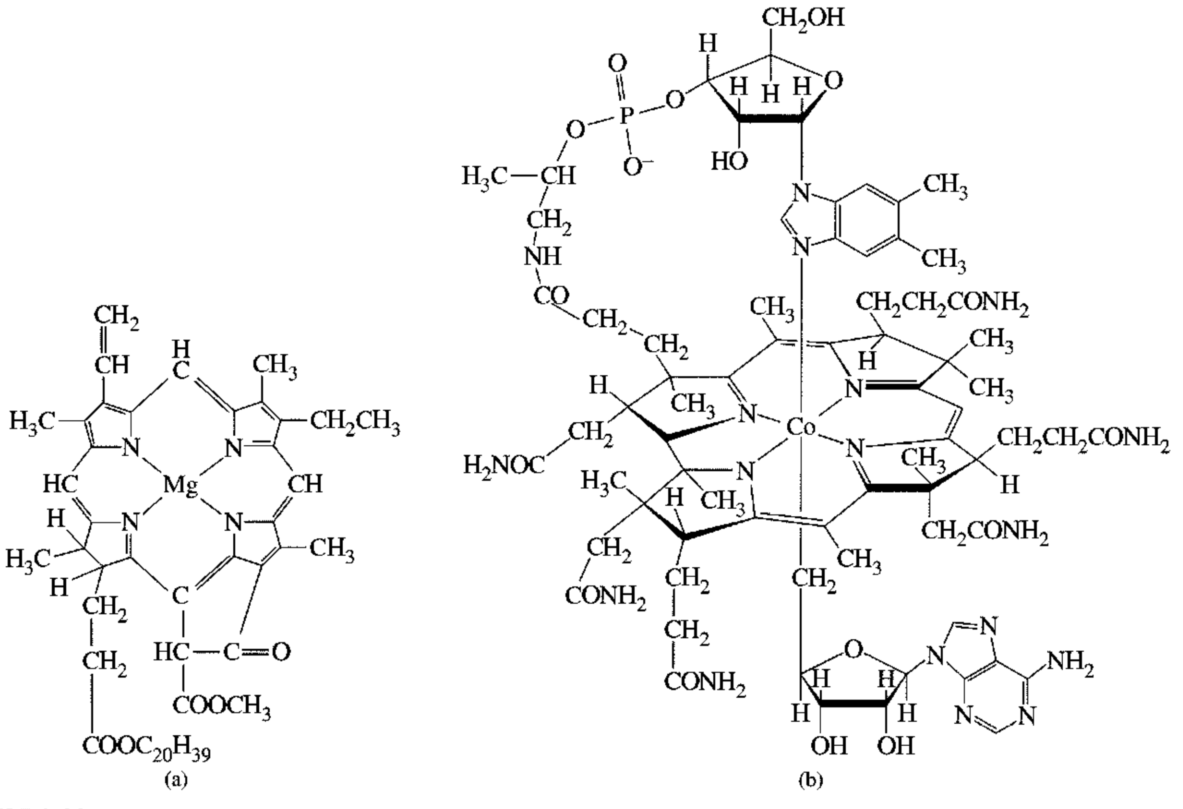
pressures than the common industrial method used up to that time. In addition, the polyethylene formed was more likely to be made up of linear rather than branched molecules and, as a consequence, was stronger and more durable. Other catalysts were soon developed, and their study contributed to the rapid expansion of organometallic chemistry, still one of the fastest growing areas of chemistry today.

The study of biological materials containing metal atoms has also progressed rapidly. Again, the development of new experimental methods allowed more thorough study of these compounds, and the related theoretical work provided connections to other areas of study. Attempts to make *model* compounds that have chemical and biological activity similar to the natural compounds have also led to many new synthetic techniques. Two of the many biological molecules that contain metals are shown in Figure 1-11. Although these molecules have very different roles, they share similar ring systems.

One current problem that bridges organometallic chemistry and bioinorganic chemistry is the conversion of nitrogen to ammonia:

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$$

This reaction is one of the most important industrial processes, with over 120 million tons of ammonia produced in 1990 worldwide. However, in spite of metal oxide catalysts introduced in the Haber-Bosch process in 1913 and improved since then, it is also a reaction that requires temperatures near 400° C and 200 atm pressure and that still results in a yield of only 15% ammonia. Bacteria, however, manage to fix nitrogen (convert it to ammonia and then to nitrite and nitrate) at 0.8 atm at room temperature in



(a) (b)

FIGURE 1-11 Biological Molecules Containing Metal Ions. (a) Chlorophyll *a*, the active agent in photosynthesis. (b) Vitamin B_{12} coenzyme, a naturally occurring organometallic compound.

nodules on the roots of legumes. The nitrogenase enzyme that catalyzes this reaction is a complex iron-molybdenum-sulfur protein. The structure of the active sites have been determined by X-ray crystallography.[11] This problem and others linking biological reactions to inorganic chemistry are described in Chapter 16.

With this brief survey of the marvelously complex field of inorganic chemistry, we now turn to the details in the remainder of this book. The topics included provide a broad introduction to the field. However, even a cursory examination of a chemical library or one of the many inorganic journals shows some important aspects of inorganic chemistry that must be omitted in a short textbook. The references cited in the text suggest resources for further study, including historical sources, texts, and reference works that can provide useful additional material.

GENERAL REFERENCES

For those interested in further discussion of the physics of the big bang and related cosmology, a nonmathematical treatment is in S. W. Hawking, *A Brief History of Time*, Bantam, New York, 1988. The title of P. A. Cox, *The Elements, Their Origin, Abundance, and Distribution*, Oxford University Press, Oxford, 1990, describes its contents exactly. The inorganic chemistry of minerals, their extraction, and their environmental impact at a level understandable to anyone with some background in chemistry can be found in J. E. Fergusson, *Inorganic Chemistry and the Earth*, Pergamon Press, Elmsford, NY, 1982. Among the many general reference works available, three of the most useful and complete are N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, Oxford, 1997; F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochman, *Advanced Inorganic Chemistry*, 6th ed., John Wiley & Sons, New York, 1999; and A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, New York, 1984. An interesting study of inorganic reactions from a different perspective can be found in G. Wulfsberg, *Principles of Descriptive Inorganic Chemistry*, Brooks/Cole, Belmont, CA, 1987.

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[11] M. K. Chan, J. Kin, and D. C. Rees, *Science*, **1993**, *260*, 792.