Cambridge University Press
978-1-107-02155-6 - Chemistry and the Environment
Sven E. Harnung and Matthew S. Johnson
Excerpt
More information

Introduction

The environment is a fascinating subject for a chemist, with a seemingly endless variety of conditions combining dramatic changes in temperature, pressure, phase, and composition. It is also an extremely useful object of study from the practical viewpoints of economy and health. Environmental chemistry is the science in which the methods and results of chemistry are applied to processes involving chemical species in the environment.[a]

Overview

More than 2,000 years ago in the Middle East, it was established that the Earth was a sphere, and the physical and chemical laws discovered since then allow the present description of the Earth as a physicochemical system. In a strictly chemical sense, the "elements" of the environment are the elements of the periodic table. However, it is convenient to add other kinds of structural units, for example, the spheres, which together with special branches of physics, for example, the laws of fluid dynamics, are needed to understand environmental systems.

Human activity

The agricultural and industrial revolutions (beginning around 1750) have allowed the human population to increase exponentially (Figure 1). In the recent past, the human population has been doubling about every 40 years, and 20 % of all humans born in the past 6,000 years are alive today. Population growth and advances in quality of life have been made possible by knowledge concerning how to use Earth's resources. Specific examples include the production of fertilizer and cement, the invention of refrigeration, medical advances, and the invention and mass production of consumer goods ranging from clothes to personal electronic devices. A key challenge facing human society today is dealing with the consequences of our success.

There are many examples of negative effects that industrial activity and population growth have had on the environment. One is an air pollution episode in London in 1952 that resulted in more than 4,000 deaths. Another is the contamination of the Arctic environment with mercury and persistent organic pollutants. Phenomena such as ozone depletion and anthropogenic climate change take place on a global scale. In order to mitigate the negative effects of humanity on the environment, it is necessary to understand how the environment works; in the end, knowledge is the key to sustainable development.

---

[a] This is not a circular definition, because the term *chemical species* is defined using more fundamental quantities.[123]

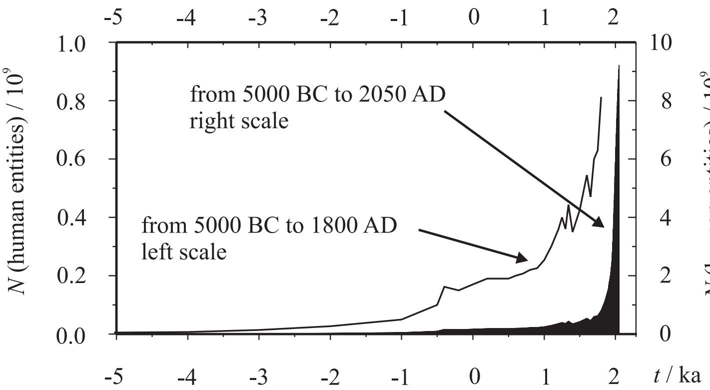


Figure 1 *Exponential growth of human population*

Human population according to the lower estimate of the U.S. Census Bureau from 5000 BC to 1850 AD (left curve), with projection to 2050 AD (right curve, which has been shaded for clarity). [a]

Some population milestones: 10 ka BC: 10^6; 6 ka BC: 10^7; 500 a BC: 10^8; 1835 AD: 10^9; 1950 AD: 2.5×10^9; 1999 AD: 6.0×10^9; 2009 AD: 6.8×10^9.

Chemistry and society

Goods and services must be produced and distributed to sustain society. This requires resources of energy and material and unavoidably affects the environment. International scientific and technical expertise is the basis for making well-founded decisions regarding energy, water, food, consumer products, industrial processes, and so forth. Here we present an outline of the structure of the international scientific organizations that manage these tasks.

A hundred years after the start of the industrial revolution the number of known chemical substances had become very large and it was no longer possible for any individual to command the entire field of chemistry. Many different systems of nomenclature were in use: chaos reigned. Therefore, an international chemical conference was organized in Karlsruhe, Germany, in 1860. The objective was to reach agreement on the theory of organic chemistry. That, in turn, required standardization of nomenclature and fundamental constants. Although the 140 chemists who attended did not reach consensus on any of the issues, committees were appointed to make recommendations, which were eventually published.

During the following years, several national chemical societies were founded,[b] and they began formulating national nomenclatures. In order to coordinate these attempts, an international conference on chemistry was held in Paris in 1889 during the World Exhibition, and here the first International Commission of Chemical Nomenclature was formed. After these preliminary steps, a series of meetings on scientific chemistry, *pure chemistry*, was organized, and in 1911 the International Association of Chemical Societies was formed.

---

[a] 5 ka BC ≈ 7 ka BP. Capital letters denote the zero of timescales: BC = before Christ, BP = before present, AD = Anno Domini (i.e., the Year of the Lord). For geological timescales, see Section 1.3.

[b] For example, The American Chemical Society 1876 and the Danish Chemical Society 1879.

During the period up to World War I, several congresses on industrial chemistry, *applied chemistry*, were held. The first was confined to sugar refining, agriculture, foodstuffs, and fermentation, but the scope of the following congresses was extended to include metallurgy, mines and explosives, electrochemistry, effluents, and chemistry applied to medicine, toxicology, pharmacy, and hygiene.

This was the background for forming the International Union of Pure and Applied Chemistry, IUPAC, in 1919 after World War I.[14,21,233] Today (2012) the union has 58 national members (i.e., chemical societies or national academies), and the work is carried out by seven divisions covering each of the major subjects of chemistry: Physical and Biophysical Chemistry, Inorganic Chemistry, Organic and Biomolecular Chemistry, Polymer Chemistry, Analytical Chemistry, Chemistry and the Environment, and Chemistry and Human Health. Eight committees have special duties including nomenclature and symbols. The coordination of the CHEMRAWN conferences will be discussed later.[a]

IUPAC is one of 31 scientific unions (2012) that are members of the International Council for Science, ICSU.[b,229] ICSU coordinates inter union projects, an example being SCOPE,[c] the Scientific Committee on Problems of the Environment. Other examples include programs aimed at collecting data on a global scale,[12,62] such as the International Polar Year, IPY,[d] and the International Geosphere-Biosphere Programme, IGBP.[e] ICSU has the important role of being the scientific advisor of the United Nations Educational, Scientific and Cultural Organization, UNESCO.

As a final illustration, in December 2008, the 63rd General Assembly of the United Nations adopted a resolution proclaiming 2011 as the International Year of Chemistry (IYC 2011). Its implementation was left to the associations: IUPAC, the chemical societies, and the national committees for chemistry.

---

[a] CHEMRAWN = Chemical Research Applied to World Needs.

[b] ICSU, founded in 1931, is the continuation of the International Research Council from 1919. Its original name was International Council of Scientific Unions, whose acronym has been preserved.

[c] See footnote *a*, Section 7.1.

[d] http://www.ipy.org (2012).

[e] http://www.igbp.net (2012).

Cambridge University Press
978-1-107-02155-6 - Chemistry and the Environment
Sven E. Harnung and Matthew S. Johnson
Excerpt
More information

1 The Earth

Since ancient times, humanity has wanted to understand the Earth. This desire has driven the development of modern physics, chemistry, geology, and biology.

Section 1.1 gives a brief survey of the present understanding of the formation of the Earth. This knowledge is based on observations of electromagnetic radiation coming from space, as well as direct observations of the Sun, the Earth, the Moon, a few planets, comets, and various meteorites found on the surface of the Earth.

In the remaining part of Chapter 1 we discuss classical results dealing with the form of the Earth, including its surface and internal structure, how its tremendous age was determined, and the important role that life has played in the development of our present environment.

1.1 Origin of the Earth

A study of environmental chemistry would not be complete without a description of the origin of the Earth and its relation to the rest of the universe. This section describes the materials of which the Earth is made, and how and why these elements are distributed among the various spheres of the Earth.

a. Big Bang

A number of observations support the theory that the present universe had an explosive start more than 10^{10} a ago. First, it was discovered that all galaxies are receding: the astronomer Hubble (1929) compiled the available data to show that the universe is expanding, implying a starting point for the expansion at about 20 Ga BP. The "Big Bang" would have given off a great deal of light as blackbody radiation, and as the universe expanded, the temperature of this radiation field would have decreased, with a simultaneous increase in the wavelength of the light.[a] The universe is still bathed in this light today, as discovered accidentally by Penzias and Wilson (1964).[102] During the testing of one of the first communication satellites, noise was detected in the microwave region of the spectrum that came from all directions in space. Subsequent research established that the temperature of the cosmic microwave radiation field depends on the direction, the mean value being 2.728 K.[b] The temperature of the

---

[a] See Section 10.1b.

[b] This value is the constant term (the monopole) of an expansion of the temperature profile onto spherical harmonic functions.

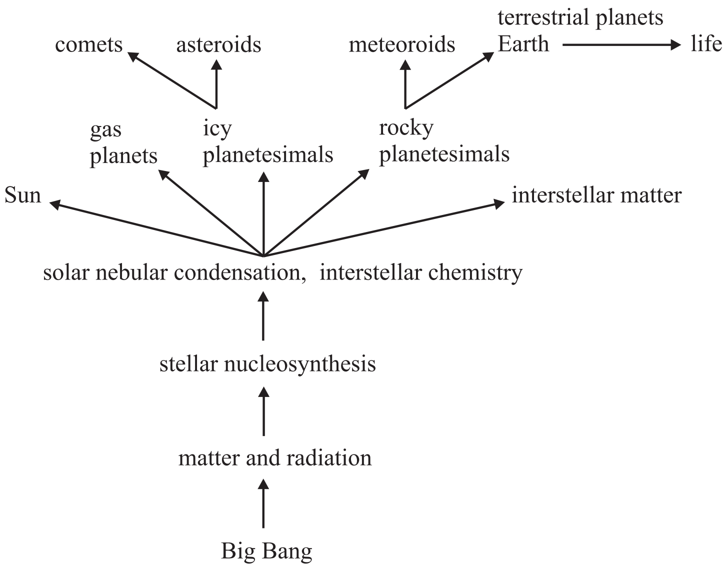


Figure 1.1 *The development of the Universe, Earth, and life*
Time proceeds upward.

young universe has been estimated by calculating backward from current conditions. At less than 10^{-4} s after the beginning, the temperature of the radiation field/plasma of matter-antimatter pairs would have been about 10^{12} K. About 10^6 a later, the temperature of the universe would have been cold enough for atoms to form. A summary of the major steps in the succeeding development is given in Figure 1.1.

The Big Bang model predicts values for the temperature and density of the universe as a function of time. When this information is combined with rates of formation of atomic nuclei from elementary particles, models show that the temperature and density of the universe between 3 and 20 minutes of age would have allowed synthesis of nuclei with atomic mass less than 5 Da. The distribution of elements is controlled by the ratio of photons to baryons, and the model predicts mole fractions of $x(^1\mathrm{H}) \approx 0.92$, $x(^4\mathrm{He}) \approx 0.08$, and smaller amounts of $^2\mathrm{H}$, $^3\mathrm{He}$, and $^3\mathrm{Li}$.

The emission and absorption of light are characteristic of specific atoms and molecules, and the compositions of celestial bodies such as stars and nebulae[a] have been determined using spectroscopy. The analysis shows that the universe does indeed contain the distribution of elements predicted by the Big Bang nucleosynthesis model, providing further verification of the theory.

Interstellar space

Table 1.1 lists more than 100 molecular entities found in interstellar space and identified using microwave spectroscopy. The kinds of entities observed are explained as resulting from the abundances of the elements (Figure 1.2) and their electronegativities (Table 1.2). Among the binary entities, one finds one fluoride, a few carbides,

---

[a] Lat. *nebula* ≙ cloud, mist.

Table 1.1 Molecular entities identified in interstellar space

Two-atomic species
H_2, CH, CH^+, CO, CO^+, CN, CS, PC, C_2, SiC, SiN, SiO, SiS, NH, NO, NS, PN, SO, SO^+, $HO^\bullet$, HCl, NaCl, KCl, AlF, AlCl

Three-atomic species
CH_2, COS, HCN, HCO, HCO^+, HCS^+, HOC^+, $HC{\equiv}C^\bullet$, C_2O, C_2S, C_3, *cyclo*-SiC_2, H_2O, H_2S, HNO, NH_2, N_2H^+, N_2O, SO_2, NaCN, NaOH, MgCN, MgNC

Four-atomic species
H_2CO, H_2CS, HNCO, HNCS, $HOCO^+$, H_2CN, $HCNH^+$, CH_2D^+, $HC{\equiv}CH$, HCCN, *cyclo*-$HC_3^\bullet$, $HC_3^\bullet$, $NC{-}C{\equiv}C^\bullet$, C_3O, C_3S, H_3O^+, NH_3

Five-atomic species
CH_4, HCOOH, $H_2C{=}NH$, $H_2N{-}CN$, CH_2CN, $H_2C{=}CO$, C_3H_2, *cyclo*-C_3H_2, $HC{\equiv}C{-}CN$, $HC{\equiv}C{-}NC$, $HC{\equiv}C{-}C{\equiv}C^\bullet$, C_5, SiH_4, SiC_4

Six-atomic species
$H_2C{=}CH_2$, CH_3CN, CH_3NC, CH_3OH, CH_3SH, $HC{\equiv}CCNH^+$, $HC{\equiv}C{-}CHO$, $HCOCH_2$, $HCONH_2$, $HC{\equiv}C{-}C{\equiv}CH$

Species with seven or more atoms
$HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C^\bullet$, $CH_2{=}CHCN$, $HC{\equiv}C{-}CH_3$, $HC{\equiv}C{-}C{\equiv}C{-}CN$, CH_3CHO, CH_3NH_2; $CH_3C{\equiv}C{-}CN$, $HC(O)OCH_3$; $CH_3{-}C{\equiv}C{-}C{\equiv}CH$, CH_3CH_2CN, $(CH_3)_2O$, CH_3CH_2OH, $HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CN$; $CH_3C{\equiv}C{-}C{\equiv}C{-}CN$, $(CH_3)_2CO$; $HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CN$; $HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CN$

Atoms and cations of metals, such as Na, K, Ca, Ti, and Fe, are not included, and more than 30 isotopologues[a] of H, N, O, Si, and S are not listed. The elements of binary compounds are ordered according to IUPAC recommendations,[124a] for example, NS instead of SN, as previously used for binary sulfur-nitrogen compounds. The list (from 2005) is growing continuously.

Table 1.2 Electronegativities of the elements listed in Table 1.1

K	Na	Ca	Mg	Al	Si	P	H	C	S	N	Cl	O	F
0.8	0.9	1.0	1.3	1.6	1.9	2.2	2.2	2.6	2.6	3.0	3.2	3.4	4.0

Pauling electronegativities, cf. inside front cover.

nitrides, and sulfides, even more chlorides, and several hydrides and oxides. Larger binary inorganic species such as $AlCl_3$ have not been observed. In contrast, the number of entities with carbon chains illustrates the remarkable ability of carbon to catenate.

It is worth noting that the terms *electropositive* and *electronegative*, referring to elements, had already been used by Berzelius in 1817.[6a] He ordered the 52 elements known at that time into a series with hydrogen in the center, in a sequence almost identical to that of the elements according to Pauling electronegativities, shown inside the front cover. Thus, these concepts are basic to an experimental chemist's

---

[a] See footnote *c*, Section 3.2c.

Cambridge University Press
978-1-107-02155-6 - Chemistry and the Environment
Sven E. Harnung and Matthew S. Johnson
Excerpt
More information

understanding of the elements. However, it is Pauling's definition (1932)[74] that stands: electronegativity is the ability of an element in a molecule to attract electrons to itself. Evidently, electronegativity is not a property of an isolated atom. Tables such as the one on the inside of the front cover are quite useful when sorting out properties of chemical species.

b. The solar system

The heavier elements in the periodic table are formed in stars and supernovae through stellar nucleosynthesis. Gravitational collapse of interstellar gas and dust during the formation of a star leads to the high densities and temperatures needed for the nuclear-synthetic reactions that give them their energy. Stars do not live forever, and supernova explosions distribute their mass into the interstellar medium; this is the so-called secondary material of the universe.

The solar system began as a spinning disk of primary and secondary material, with the protosun at its center. The pioneering isotope chemist Harold Urey wrote in 1952 that the primary mechanism fractionating material during the formation of a solar system is the separation of dust from gas. A young star ejects large amounts of ions and particles called the solar wind, which blows gas away from the center of the disk. The outward pressure is counteracted by the gravitational attraction of the star. Different types of material respond differently to these opposing forces, depending on each material's charge, mass, and collision cross section. Because of the temperature gradient inward to the star, the composition of the dust varies from containing only refractory[a] material near the center to containing semivolatile material farther out in the disk.

Before continuing the discussion of the partitioning of material in the solar nebula, we look at the (high-temperature) geochemical classification of the elements.

Abundances and classification of the elements

Analysis of spectroscopic data has provided information about the distribution of elements in the Sun (see Figure 1.2).[149] Data of this type have been critical for developing theories of nucleosynthesis in stars. A closer inspection of the figure shows an odd-even variation: elements with an even atomic number Z are generally more abundant than the adjacent odd-Z elements. This fact has been explained in terms of a stable nuclear structure (Harkins, 1917 and 1931; Goeppert-Mayer, 1948). Another feature of stellar nucleosynthesis is that nuclei whose mass number (sum of protons and neutrons) is a multiple of 4 are typically very stable, and these elements are the main components of the Earth.

Ninety-one elements occur naturally on the Earth, namely, the elements from ${}_{1}$H to ${}_{92}$U, minus ${}_{43}$Tc and ${}_{61}$Pm, plus ${}_{94}$Pu, which has been found in uranium ores from southern California.[b] By mass, half of the mantle is ^{16}O and one-fourth ^{28}Si. In all,

---

[a] The term *refractory* refers to the ability of a chemical species to retain its structure and physical strength at high temperature.

[b] The nomenclature of indices around an element symbol is given in Appendix A1.

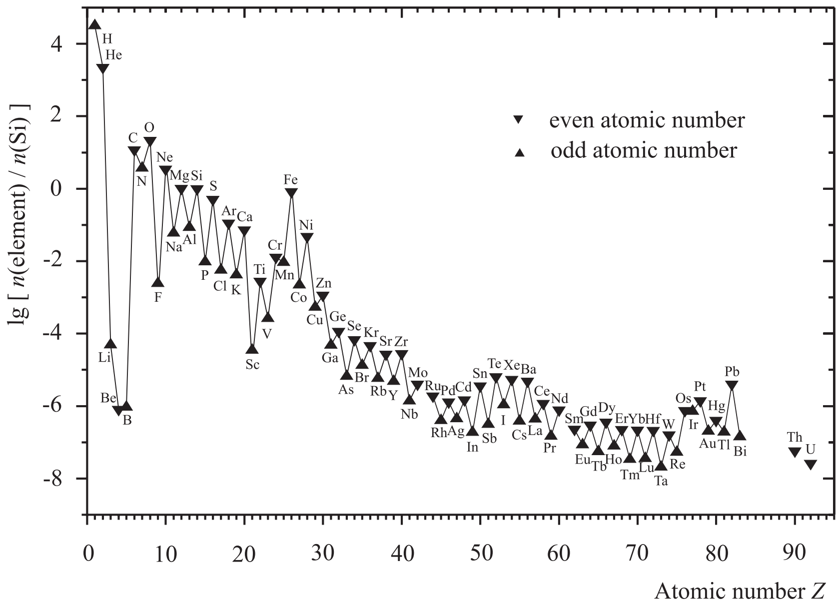


Figure 1.2 *Solar abundance of the elements as a function of atomic number*[149]
The logarithm of the abundance of the elements relative to that of Si as found in the Sun. Meteorites provide abundance data for nonvolatile elements as well; their abundances differ by at most a factor of 3 from those of the Sun.

the four nuclides ^{16}O, ^{24}Mg, ^{28}Si, and ^{56}Fe make up 85 % of the mass of Earth. A few other nuclides with mass number divisible by four, ^{12}C, ^{32}S, ^{40}Ca, and ^{48}Ti are also key components. If we add ^{23}Na, ^{27}Al, and ^{39}K to the list, we have accounted for 99 % of the mass of the mantle of the Earth (see Section 1.2).

While analyzing an earthquake, Mohorovičić (1909) saw that the velocity of seismic waves changed with depth (seismic discontinuities; see Section 1.2b). This observation eventually led to an increased understanding of the chemical structure of the interior of the planet: the change from a light silica-alumina (sial) rich crust to a silica-magnesia (sima) rich mantle resting on a dense nickel-iron (nife) core.

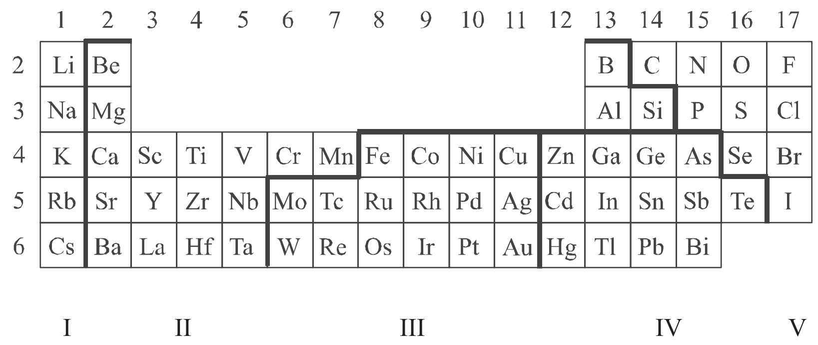
Such observations gave rise to the geochemical classification[168] of the elements, shown in Figure 1.3 (Goldschmidt, 1937).[c] The original discussion was concerned with partition equilibria of the elements among liquid iron (rich in free electrons), liquid sulfides (of semimetallic nature), and fused silicates (ionic liquid). When taken in the context of a cooling protoplanet, the classification gains substantially in chemical significance. Elements soluble in molten iron are called siderophiles; those with an affinity for molten sulfides, chalcophiles; and those prefering liquid silicates, lithophiles.[d]

Figure 1.3 shows the geochemical classification of periods 2 through 6 of the periodic table. Classes I through V are distinguished in the following discussion. In general, classes I through IV comprise the metals (the electropositive elements) and

---

[c] Goldschmidt's discussion[168] included atmophilic elements (Table 3.18) and biophilic elements (Table 3.26).

[d] Gk. *λιθος* ≙ stone; *σιδηρο-* ≙ iron-; *χαλκ*= ore; *φιλο* − ≙ loving-; *γενναω* ≙ form.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
2	Li	Be											B	C	N	O	F
3	Na	Mg											Al	Si	P	S	Cl
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		

Figure 1.3 *Geochemical classification of selected elements*

I Lithophiles; volatile metals; moderately refractory oxides.
II Lithophiles; refractory oxides; the group includes Th and U; the transition metals V, Cr, and Mn are moderately oxyphilic elements.
III Siderophiles; the group includes C and P. Note that Tc has no stable isotopes.
IV Chalcophilic and volatile elements; the group includes S and Se.
V Nonmetals.

class V the nonmetals (the electronegative elements). The elements of classes I and II are lithophiles; those of class I form moderately refractory oxides [$\theta_{\text{fus}}(\text{Na}_2\text{O}) = 1132\ ^\circ\text{C}$, $\theta_{\text{fus}}(\text{K}_2\text{O}) > 740\ ^\circ\text{C}$],[a] whereas the oxides of class II are refractory with high melting points [$\theta_{\text{fus}}(\text{MgO}) = 2826\ ^\circ\text{C}$; $\theta_{\text{fus}}(\text{Al}_2\text{O}_3) = 2054\ ^\circ\text{C}$]. The siderophilic elements (class III + C + P) are those that have an affinity for liquid iron [$\theta_{\text{fus}}(\text{Fe}) = 1538\ ^\circ\text{C}$, $\theta_{\text{vap}}(\text{Fe}) = 2861^\circ\text{C}$]; at lower temperatures, they form sulfides. Class IV comprises the chalcophiles: that is, the elements that have an affinity for the elements of group 16.[b] Some of elements of class IV are quite volatile [$\theta_{\text{vap}}(\text{Hg}) = 357\ ^\circ\text{C}$]. The limits between the groups are not sharp; for example, the sulfides of the coinage metals (Cu, Ag, and Au) are somewhat soluble in molten class IV sulfides, and in Nature these elements are found as sulfides and in the pure state.

Compositions of the planets

The compositions of the planets are functions of chemical and physical mechanisms. The inner planets are almost completely composed of refractory compounds and siderophilic elements, whereas the outer planets are made of gas around a rocky core. The three planets Venus, Earth, and Mars were formed by similar processes and together are known as the terrestrial planets; some data are given in Table 1.3. Rocks from the Moon brought back by the Apollo and Luna missions show a mineral composition not found on Earth; the Moon is believed to have been formed by a bolide collision with the Earth. In contrast to the gas giants Jupiter and Saturn,[c] the terrestrial planets are not massive enough to have attracted a significant atmosphere

---

[a] θ_{fus} denotes the temperature of fusion (solid → liquid); θ_{vap} denotes the temperature of vaporization (liquid → gas).[126]

[b] The chalcogens are the elements that form ores, that is, group 16.

[c] Jupiter: mass = 1.899×10^6 Yg, density = 1.33 g cm^{-3}.
Saturn: mass = 0.569×10^6 Yg, density = 0.70 g cm^{-3}.

Table 1.3 Some properties of the terrestrial planets[129]

	Venus ♀	Earth ⊕	Mars ♂
Mass / Yg [1]	4869.0	5957.4	641.9
Radius / km [1]	6051.9	6366.7	3397
Gravity / m s^{-2}	8.87	9.80	1.62
Density / g cm^{-3}	5.24	5.51	3.94
Escape velocity / km s^{-1}	10.4	11.2	2.37
Distance to Sun / au [2]	0.723	1	1.524
Albedo [3]	0.65	0.30	0.15
T_s / K [4]	730	287	218
p_s / bar [5]	90	1.013	0.007
Atmospheric composition as mole fraction:			
CO_2	0.964	380×10^{-6}	0.9532
N_2	0.034	0.7808	0.027
O_2	69×10^{-6}	0.2095	0.0013
H_2O	0.001	0 to 0.03	300×10^{-6}
Ar	4×10^{-6}	0.0093	0.016
Ne	–	18×10^{-6}	3×10^{-6}
CO	20×10^{-6}	1×10^{-6}	0.0007

[1] See the discussion at Table 1.5.
[2] The astronomical unit: 1 au = 149.6 Gm.
[3] See Section 10.1c.
[4] Mean surface temperature.
[5] Surface pressure.

of primary material, gas trapped by the gravitational potential of the planet. Instead, their atmospheres are secondary, resulting from the outgassing of the material from which the planet is made. One indication that Earth has a secondary atmosphere is that the relative abundance of He in the atmosphere is 10^{14} less than in the Sun or the universe as a whole.

Material originating with the formation of the solar nebula can be found in a special class of meteorites called carbonaceous chondrites. These meteorites are made of grains of material that are believed to have condensed directly from gaseous material in the solar nebula. This condensation likely took place within 50 ka of the formation of the disk, about 4.6 Ga BP. The relative abundances of many of the elements in these meteorites are about the same as the abundances found in the Sun, (see Figure 1.2).

c. The Earth

Condensation of the solar nebula

Urey's description of processes in the solar nebula aims to account for the chemical compositions of the planets and their densities based on the assumption that the initial