

PRINCIPLES OF
**MODERN
CHEMISTRY**

FOURTH EDITION

OXToby

GILLIS

NACHTRIEB

VIII

AMEREN UE EXHIBIT 1040
Page 2

Physical Constants

Standard acceleration of terrestrial gravity	$g = 9.80655 \text{ m s}^{-2}$ (exactly)
Avogadro's number	$N_0 = 6.022137 \times 10^{23}$
Bohr radius	$a_0 = 0.52917725 \text{ \AA} = 5.2917725 \times 10^{-11} \text{ m}$
Boltzmann's constant	$k_B = 1.38066 \times 10^{-23} \text{ J K}^{-1}$
Electron charge	$e = 1.6021773 \times 10^{-19} \text{ C}$
Faraday constant	$\mathcal{F} = 96,485.31 \text{ C mol}^{-1}$
Masses of fundamental particles:	
Electron	$m_e = 9.109390 \times 10^{-31} \text{ kg}$
Proton	$m_p = 1.672623 \times 10^{-27} \text{ kg}$
Neutron	$m_n = 1.674929 \times 10^{-27} \text{ kg}$
Ratio of proton mass to electron mass	$m_p/m_e = 1836.15270$
Permittivity of vacuum	$\epsilon_0 = 8.8541878 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$
Planck's constant	$h = 6.626076 \times 10^{-34} \text{ J s}$
Speed of light in a vacuum	$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$ (exactly)
Universal gas constant	$R = 8.31451 \text{ J mol}^{-1} \text{ K}^{-1}$ $= 0.0820578 \text{ L atm mol}^{-1} \text{ K}^{-1}$

Values are taken from *Quantities, Units and Symbols in Physical Chemistry*, International Union of Pure and Applied Chemistry, Blackwell Scientific Publications, 1988.

Conversion Factors

Standard atmosphere	$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$ $= 1.01325 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2}$ (exactly)
Atomic mass unit	$1 \text{ u} = 1.660540 \times 10^{-27} \text{ kg}$ $1 \text{ u} = 1.492419 \times 10^{-10} \text{ J} = 931.4943 \text{ MeV}$ (energy equivalent from $E = mc^2$)
Calorie	$1 \text{ cal} = 4.184 \text{ J}$ (exactly)
Electron volt	$1 \text{ eV} = 1.6021773 \times 10^{-19} \text{ J}$ $= 96.48531 \text{ kJ mol}^{-1}$
Foot	$1 \text{ ft} = 12 \text{ in} = 0.3048 \text{ m}$ (exactly)
Gallon (U.S.)	$1 \text{ gallon} = 4 \text{ quarts} = 3.78541 \text{ L}$ (exactly)
Liter-atmosphere	$1 \text{ L atm} = 101.325 \text{ J}$ (exactly)
Metric ton	$1 \text{ metric ton} = 1000 \text{ kg}$ (exactly)
Pound	$1 \text{ lb} = 16 \text{ oz} = 0.45359237 \text{ kg}$ (exactly)

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TO THE MEMORY OF NORMAN NACHTRIEB, OUR TEACHER, COLLEAGUE, AND
FRIEND, WHOSE MANY CONTRIBUTIONS FILL THIS BOOK AND WHOSE SPIRIT
CONTINUES TO INSPIRE US.

*The search for truth is in one way hard and in another easy,
for it is evident that no one can master it fully or miss it completely.
But each adds a little to our knowledge of nature, and from all
the facts assembled there arises a certain grandeur.*

(Greek inscription, taken from Aristotle, on the facade of
the National Academy of Sciences building in Washington, D.C.)

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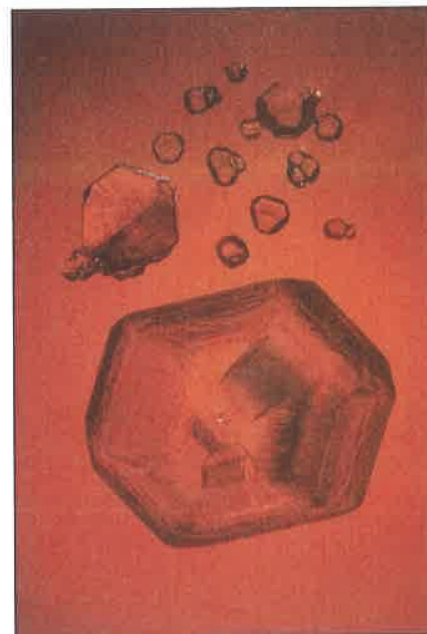
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Crystals of alum.

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Ice and water.

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increasing atomic number Z , these families display a remarkable fact: patterns of chemical behavior recur regularly as a function of Z . This discovery is summarized concisely by **the periodic law**:

The chemical properties of the elements are periodic functions of the atomic number Z .

Consequently the elements listed in order of increasing Z can be arranged in a chart called the **periodic table** that displays at a glance the patterns of chemical similarity. The periodic table then permits systematic classification, interpretation, and prediction of all chemical information.

The modern periodic table, shown in Figure 1.11 and inside the front cover of this book, places elements in **groups** (arranged vertically) and **periods** (arranged horizontally). There are eight groups of **representative elements** or “main-group” elements. In addition, there are ten groups (and three periods) of **transition-metal elements**, a period of elements from atomic number 57 through 71 called the rare-earth or **lanthanide elements**, and a period of elements from atomic number 89 through 103 called the **actinides**, all of which are unstable and most of which must be produced artificially. The lanthanide and actinide elements are usually placed below the rest of the table to conserve space. The groups of representative elements are numbered (with Roman numerals) from I to VIII, with the letter A sometimes added to differentiate them from the transition-metal groups, which are labeled from IB to VIIIB. In this book we will use group numbers exclusively for the representative elements (dropping the “A”), and we will refer to transition-metal elements by the first element in the corresponding group. For example, the elements in the carbon group (C, Si, Ge, Sn, Pb) are designated as Group IV, and the elements chromium (Cr), molybdenum (Mo), and tungsten (W) as the chromium group.³

Survey of Chemical Properties: The Representative Elements

Empirical classification of the elements is based on similarities in physical or chemical properties. Elements are classified as **metals** or **nonmetals**, depending on the presence (or absence) of a characteristic metallic luster, good (or poor) ability to conduct electricity and heat, and malleability (or brittleness). Certain elements (antimony, arsenic, boron, silicon, and tellurium) resemble metals in some respects and nonmetals in others and are therefore called **semimetals** or **metalloids**. Empirical formulas of the binary compounds of the elements with chlorine (their *chlorides*), with oxygen (their *oxides*), and with hydrogen (their *hydrides*), reveal chemical periodicity.

Group I, the **alkali metals** (lithium, sodium, potassium, rubidium, and cesium), are all relatively soft metals with low melting points that form 1:1 compounds with chlorine, having chemical formulas such as NaCl and RbCl. The alkali metals react with water to liberate hydrogen; potassium, rubidium, and cesium liberate sufficient heat of reaction to ignite the hydrogen. Group II, the **alkaline-earth metals** (beryllium, magnesium, calcium, strontium, barium, and radium), react in a 1:2 atom ratio with chlorine, giving compounds such as MgCl_2 and CaCl_2 .

Of the nonmetallic elements, Group VI, the **chalcogens** (oxygen, sulfur, selenium, and tellurium), form 1:1 compounds with alkaline-earth metals (e.g., CaO

³ Recently, several international organizations recommended a new system of group designation in which the main-group elements make up Groups 1, 2, and 13 through 18, and the transition-metal elements fill Groups 3 through 12.

PERIOD

1	1 I H 1766	2 II He 1895	TRANSITION ELEMENTS										13 III B 1808	14 IV C 1772	15 V N 1772	16 VI O 1772	17 VII F 1887	18 VIII Ne 1898
2	3 Li 1817	4 Be 1798											5 Al 1827	6 Si 1823	7 P 1669	8 S 1774	9 Cl 1774	10 Ar 1894
3	11 Na 1807	12 Mg 1756	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 Al 1827	14 Si 1823	15 P 1669	16 S 1774	17 Cl 1774	18 Ar 1894
4	19 K 1807	20 Ca 1808	21 Sc 1879	22 Ti 1791	23 V 1830	24 Cr 1797	25 Mn 1774	26 Fe 1735	27 Co 1751	28 Ni 1751	29 Cu 1746	30 Zn 1746	31 Ga 1875	32 Ge 1886	33 As 1817	34 Se 1817	35 Br 1826	36 Kr 1898
5	37 Rb 1861	38 Sr 1790	39 Y 1794	40 Zr 1789	41 Nb 1801	42 Mo 1778	43 Tc 1937	44 Ru 1844	45 Rh 1803	46 Pd 1803	47 Ag 1817	48 Cd 1817	49 In 1863	50 Sn 1782	51 Sb 1782	52 Te 1782	53 I 1811	54 Xe 1898
6	55 Cs 1860	56 Ba 1808	71 Lu 1907	72 Hf 1923	73 Ta 1802	74 W 1781	75 Re 1925	76 Os 1803	77 Ir 1803	78 Pt 1735	79 Au 1861	80 Hg 1861	81 Tl 1861	82 Pb 1886	83 Bi 1886	84 Po 1898	85 At 1940	86 Rn 1900
7	87 Fr 1939	88 Ra 1898	103 Lr 1961	104 Rf 1965	105 Db 1970	106 Sg 1976	107 Bh 1976	108 Hs 1984	109 Mt 1982	110 Uun 1994	111 Uuu 1994							

LANTHANIDES

57 La 1839	58 Ce 1803	59 Pr 1885	60 Nd 1843	61 Pm 1947	62 Sm 1879	63 Eu 1896	64 Gd 1880	65 Tb 1843	66 Dy 1886	67 Ho 1879	68 Er 1843	69 Tm 1879	70 Yb 1907
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ACTINIDES

89 Ac 1899	90 Th 1828	91 Pa 1917	92 U 1789	93 Np 1940	94 Pu 1940	95 Am 1945	96 Cm 1944	97 Bk 1950	98 Cf 1950	99 Es 1952	100 Fm 1953	101 Md 1955	102 No 1958
------------------	------------------	------------------	-----------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	-------------------	-------------------	-------------------

Abundances by mass

> 0.1%	0.0001–0.001%
0.01–0.1%	10 ⁻⁶ –10 ⁻⁴ %
0.001–0.01%	< 10 ⁻⁶ %

FIGURE 1.11 The modern periodic table of the elements. Below each symbol is the year in which that element was discovered; elements with

FIGURE 1.11 The modern periodic table of the elements. Below each symbol is the year in which that element was discovered; elements with no dates have been known since ancient times. Above each symbol is the atomic number. The color coding indicates the relative abundance by mass of the elements in the world (the atmosphere, oceans and fresh-water bodies, and the Earth's crust to a depth of 40 km). Oxygen alone comprises almost 50% of this mass, and silicon comprises more than 25%.

and BaS) but 2:1 compounds with the alkali metals (e.g., Li_2O and Na_2S). Members of Group VII, the **halogens** (fluorine, chlorine, bromine, and iodine) differ significantly in physical properties (the first two are gases at room temperature, bromine is a liquid, and iodine a solid), but their chemical behaviors are similar. Any alkali-metal element will combine with any halogen in 1:1 proportion to form a compound such as LiF or RbI , called an **alkali halide**. Alkaline-earth metals react with halogens in 1:2 proportion, giving alkaline-earth halides such as CaF_2 and MgBr_2 .

Other elements fall into three additional groups that are somewhat less clearly defined in their chemical and physical properties than those already mentioned. Group III contains a semimetal (boron) and four metals (aluminum, gallium, indium, and thallium). All form 1:3 chlorides (such as GaCl_3) and 2:3 oxides (such as Al_2O_3). Group IV consists of the elements carbon, silicon, germanium, tin, and lead. All of these elements form 1:4 chlorides (such as SiCl_4), 1:4 hydrides (such as GeH_4), and 1:2 oxides (such as SnO_2). Tin and lead are metals with low melting points, and silicon and germanium are semimetals. Elemental carbon exists in numerous forms: graphite, diamond, and the recently discovered fullerenes. Group V includes nitrogen, phosphorus, arsenic, antimony, and bismuth. With hydrogen and oxygen these

elements form binary compounds with empirical formulas such as PH_3 and N_2O_5 . The hydrides become increasingly unstable as their molar masses increase, and BiH_3 can only be kept below -45°C . A similar trend exists for the oxides, and Bi_2O_5 has never been obtained in pure form. The lighter members of this group are clearly nonmetals (nitrogen and phosphorus)—bismuth is clearly a metal—and arsenic and antimony are classed as semimetals.

Group VIII, the noble gases (helium, neon, argon, krypton, xenon, and radon), are sometimes called the **inert gases** because of their relative inertness toward chemical combination. These all appear in monatomic form, unlike the other permanent gases (hydrogen, oxygen, nitrogen, fluorine, chlorine) which are diatomic.

Survey of Physical Properties

Physical as well as chemical properties of the elements vary systematically across the periodic table. Important physical properties include melting points and boiling points, thermal and electrical conductivities, densities, atomic sizes, and the energy changes involved in adding an electron to or removing an electron from a neutral atom. Appendix F presents numerical values for most of these properties. In general, the elements on the left side of the table (especially in the later periods) are metallic solids and good conductors of electricity. On the right side (especially in earlier periods) they are poor conductors of electricity and are generally found in the gaseous state at room temperature. In between, the semimetals form a zigzag line of division between metallic and nonmetallic elements (see inside the front cover of this book).

Patterns in chemical reactivity of the elements, evidenced by the arrangement of the groups and periods in the table, correlate with patterns in the physical structure of the atom, evidenced by Z . Reading across the table horizontally shows that each main group element (Groups I–VIII) in Period 3 contains exactly 8 more electrons than the element immediately above it. Similarly, each main group element in Periods 4 and 5 contains exactly 18 more electrons than the element immediately above it. The explanation why increasing Z by 8 in period 2 and increasing Z by 18 in periods 3 and 4 produces similar chemical reactivity will be provided by the quantum mechanical theory of atomic structure in Chapter 15.

Development of the Periodic Table

The periodic table is a monumental scientific achievement. Its development is a fascinating story which illustrates the essential interplay between observation, prediction, and testing required for scientific progress. By the late 1860s more than 60 chemical elements had been identified, and much was known about their descriptive chemistry. Various proposals were put forth to arrange the elements into groups based on similarities in chemical and physical properties. The next step was to recognize a connection between group properties and atomic masses. When the elements known at the time were written in order of increasing atomic mass, repetitive sequences of the groups appeared. When the series of elements was written so as to begin a new row with each alkali metal, elements of the same groups were automatically assembled in columns in a periodic table of the elements that was the forerunner of the modern table.

When the German chemist Lothar Meyer and (independently) the Russian Dmitri Mendeleev first introduced the periodic table in 1869–70, one third of the

naturally occurring chemical elements had not yet been discovered. Yet both chemists were sufficiently farsighted to leave gaps where their analyses of periodic physical and chemical properties indicated that new elements should be located. Mendeleev was bolder than Meyer and even assumed that if a measured atomic mass put an element in the wrong place in the table, the atomic mass was wrong. In some cases this was true. Indium, for example, had previously been assigned an atomic mass between those of arsenic and selenium. Because there is no space in the periodic table between these two elements, Mendeleev suggested that the atomic mass of indium be changed to a completely different value, where it would fill an empty space between cadmium and tin. Subsequent work has shown that the elements are *not* ordered strictly by atomic mass in the periodic system. For example, tellurium comes before iodine in the periodic table, even though its atomic mass is slightly greater. Such anomalies are due to the relative abundances of the isotopes of the elements involved. We now know (Section 1.4) that atomic number, not mass number, determines chemical behavior.

Mendeleev went further than Meyer in another respect: he predicted the properties of six elements yet to be discovered. For example, a gap just below aluminum suggested a new element would be found with properties analogous to those of aluminum. Mendeleev designated this element “eka-aluminum” (Sanskrit *eka*, “next”) and predicted its properties. Just five years later an element with the proper atomic mass was isolated and named *gallium* by its discoverer. The close correspondence between the observed properties of gallium and Mendeleev’s predictions for eka-aluminum lent strong support to the periodic law. Additional support came in 1885 when eka-silicon, which had also been described in advance by Mendeleev, was discovered and named *germanium*.

The structure of the periodic table appeared to limit the number of possible elements. It was therefore quite surprising when John William Strutt, Lord Rayleigh, discovered a gaseous element in 1894 that did not fit into the previous classification scheme. A century earlier, Henry Cavendish had noted the existence of a residual gas when oxygen and nitrogen are removed from air, but its importance had not been realized. Together with William Ramsay, Rayleigh isolated the gas and named it argon. Ramsay then studied a gas that was present in natural gas deposits and discovered that it was helium, an element whose presence in the sun had been noted earlier in the spectrum of sunlight but that had not previously been known on Earth. Rayleigh and Ramsay postulated the existence of a new group of elements, and in 1898 other members of the series (neon, krypton, and xenon) were isolated.

1.6

THE MOLE CONCEPT: WEIGHING AND COUNTING MOLECULES

The laws of chemical combination assert that chemical reactions occur not through arbitrary amounts of material but by regrouping atoms in numbers specific to the substances involved in the reaction. How does one weigh out a sample containing exactly the number of atoms or molecules needed for a particular chemical reaction? What is the mass of an atom or a molecule? These questions must be answered indirectly, since atoms and molecules are far too small to permit direct determination of their masses.

While developing the laws of chemical combination, chemists had determined indirectly the relative masses of atoms of different elements; for example, 19th-century chemists concluded that oxygen atoms weigh 16 times more than hydrogen atoms. In the early 20th century, atomic and molecular relative masses were determined much more accurately by the work of J. J. Thomson, F. W. Aston, and others who developed the technique of **mass spectrometry** as an extension of Thomson's measurement of the charge-mass ratio of the electron. These relative masses on the atomic scale are related to absolute masses on the gram scale through a conversion factor. Finally, one weighs out a sample of the mass required to provide the desired number of atoms or molecules of a substance for a particular reaction. These concepts and methods are developed in the present section.

Direct Physical Measurements of Relative Atomic and Molecular Masses: Mass Spectrometry

Mass spectrometry is the chemist's most accurate method for determining relative atomic and molecular masses. In a mass spectrometer (Fig. 1.12), one or more electrons are removed from each such atom or molecule. The resulting positively charged species, called **ions**, are accelerated by an electric field then passed through a magnetic field. The extent of curvature of the particle trajectories depends on the ratio of their charges to their masses, just as in Thomson's experiments on cathode rays (electrons) described in Section 1.4. This technique allows species of different mass to be separated and detected. Early experiments in mass spectrometry demon-

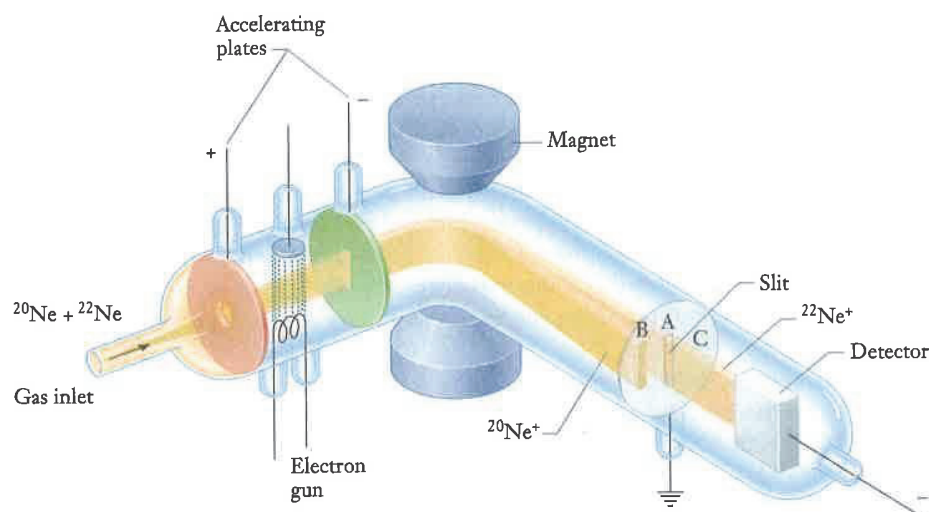


FIGURE 1.12 A simplified representation of a modern mass spectrometer. A gas mixture containing the isotopes ^{20}Ne and ^{22}Ne is introduced through the gas inlet. Some of these atoms are ionized by collisions with electrons as they pass through the electron gun. The resulting ions are accelerated to a particular kinetic energy by the electric field between the accelerating plates. The ion beam passes into a magnetic field, where it is separated into components, each containing ions with a characteristic charge-to-mass ratio. Here, the spectrometer has been adjusted to detect the less strongly deflected $^{22}\text{Ne}^+$ ions in the inlet mixture. By changing the magnitude of the electric or magnetic field, one can move the beam of $^{20}\text{Ne}^+$ ions from B to A, and the beam of $^{22}\text{Ne}^+$ ions from B to C, so that $^{20}\text{Ne}^+$ ions can be detected.

strated, for example, a mass ratio of 16:1 for oxygen relative to hydrogen, confirming by *physical* techniques a relationship deduced originally on *chemical* grounds.

Because many elements have more than one naturally occurring isotope, however, the relationship between the chemist's and the physicist's relative atomic masses was not always so simple. The atomic mass of chlorine determined by chemical means was 35.45 (relative to an oxygen atomic mass of 16), but instead of showing a single peak in the mass spectrum corresponding to a relative atomic mass of 35.45, chlorine showed two peaks, with relative masses near 35 and 37. Approximately three quarters of all chlorine atoms appear to have relative atomic mass 35 (the ^{35}Cl atoms), and one quarter have relative atomic mass 37 (the ^{37}Cl atoms). Naturally occurring chlorine is thus a mixture of two isotopes with different masses but very nearly identical chemical properties. Elements in nature usually are mixtures, after all. Dalton's second assumption (that all atoms of a given element are identical in mass) is thus shown to be wrong in most cases. Because the *chemical* properties of different isotopes are so similar, their existence was not discovered until the development of the mass spectrometer.

Until 1900 chemists worked with a scale of relative atomic masses in which the average relative atomic mass of hydrogen was set at 1. At about that time, they changed to a scale in which the average relative atomic mass of naturally occurring oxygen (a mixture of ^{16}O , ^{17}O , and ^{18}O) was set at 16. In 1961, by international agreement, the atomic mass scale was further revised, with the adoption of exactly 12 as the relative atomic mass of ^{12}C . There are two stable isotopes of carbon: ^{12}C and ^{13}C (^{14}C and other isotopes of carbon are unstable and of very low terrestrial abundance). Natural carbon contains 98.892% ^{12}C and 1.108% ^{13}C by mass. The relative atomic masses of the elements as found in nature can be obtained as averages over the masses of the isotopes of each element, weighted by their observed fractional abundances. If an element consists of n isotopes, of which the i th isotope has a mass A_i and a fractional abundance p_i , then the average relative atomic mass of the element in nature (its chemical relative atomic mass) will be

$$A = A_1p_1 + A_2p_2 + \cdots + A_np_n \equiv \sum_{i=1}^n A_ip_i \quad [1.1]$$

The relative atomic mass of a nuclide is close to but (except for ^{12}C) not exactly equal to its mass number.

EXAMPLE 1.3

Calculate the chemical relative atomic mass of carbon, taking the relative atomic mass of ^{13}C to be 13.003354 on the ^{12}C scale.

Solution

Set up the following table:

Isotope	Isotopic Mass $\times$ Abundance
^{12}C	$12.000000 \times 0.98892 = 11.867$
^{13}C	$13.003354 \times 0.01108 = 0.144$
Chemical relative atomic mass = 12.011	

Related Problems: 23, 24, 25, 26

The number of significant figures in a table of chemical or natural relative atomic masses (see inside the back cover of this book) is limited not only by the accuracy of the mass spectrometric data but also by any variability in the natural abundances of the isotopes. If lead from one mine has a relative atomic mass of 207.18 and lead from another has 207.23, there is no way a result more precise than 207.2 can be obtained. In fact, geochemists now are able to use small variations in the ^{16}O : ^{18}O isotopic abundance ratio as a "thermometer" to deduce the temperatures at which different oxygen-containing rocks were formed in the Earth's crust over geologic time scales. They also find anomalies in the oxygen isotopic compositions of certain meteorites, implying that their origins may lie outside our solar system.

Relative atomic masses have no units because they are ratios of two masses measured in whatever units we choose (grams, kilograms, pounds, and so forth). The **relative molecular mass** of a compound is the sum of the relative atomic masses of the elements that constitute it, each one multiplied by the number of atoms of that element in a molecule. The formula of water is H_2O , for example, so its relative molecular mass is

$$2 (\text{relative atomic mass of H}) + 1 (\text{relative atomic mass of O}) = 2(1.0079) + 1(15.9994) = 18.0152$$

Relation of Atomic and Macroscopic Masses: Avogadro's Number

What are the actual masses (in grams) of individual atoms and molecules? To answer this, it is necessary to establish a connection between the macroscopic scale of masses used in the laboratory and the microscopic scale of the masses of individual atoms and molecules. The link between the two is provided by **Avogadro's number** (N_0), defined as the number of atoms in exactly 12 g of ^{12}C . We will later consider some of the many experimental methods that have been developed to determine the numerical value of N_0 . Its currently accepted value is

$$N_0 = 6.022137 \times 10^{23}$$

The mass of a single ^{12}C atom is then found by dividing exactly 12 g by N_0 :

$$\text{mass of a } ^{12}\text{C} = \frac{12.0000 \text{ g}}{6.022137 \times 10^{23}} = 1.992648 \times 10^{-23} \text{ g}$$

This is truly a very small mass, reflecting the very large number of atoms in a 12-g sample of carbon.

Avogadro's number is defined relative to the ^{12}C atom because that isotope is the basis for the modern scale of relative atomic masses. We can apply it to other substances as well, in a particularly simple fashion. Consider sodium, which has a relative atomic mass of 22.98977. A sodium atom is 22.98977/12 times as heavy as a ^{12}C atom. If N_0 atoms of ^{12}C have a mass of 12 g, then the mass of N_0 atoms of sodium must be

$$\frac{22.98977}{12} (12 \text{ g}) = 22.98977 \text{ g}$$

The mass, in grams, of N_0 atoms of *any* element is numerically equal to the relative atomic mass of that element. The same conclusion applies to molecules. From the relative molecular mass of water calculated earlier, the mass of N_0 molecules of water is 18.0152 g.

EXAMPLE 1.4

One of the heaviest atoms found in nature is ^{238}U . It has a relative atomic mass of 238.0508 on a scale in which 12 is the atomic mass of ^{12}C . Calculate the mass (in grams) of one atom of ^{238}U .

Solution

Because N_0 atoms of ^{238}U have a mass of 238.0508 g and N_0 is 6.022137×10^{23} , one atom must have a mass equal to

$$\frac{238.0508 \text{ g}}{6.022137 \times 10^{23}} = 3.952929 \times 10^{-22} \text{ g}$$

Related Problems: 27, 28

The Mole Concept

Atoms and molecules have very small masses, so chemical experiments with measurable amounts of substances involve many of these atoms and molecules. It is convenient to group atoms or molecules in counting units of $N_0 = 6.022137 \times 10^{23}$ to measure the **chemical amount** of a substance. One of these counting units is called a **mole** (abbreviated “mol”; from Latin *moles*, meaning “heap” or “pile”). One mole of a substance is the amount that contains Avogadro’s number of atoms, molecules, or other entities. In other words, 1 mol of ^{12}C contains N_0 ^{12}C atoms, 1 mol of water contains N_0 water molecules, and so forth. We must be careful in some cases, because a phrase such as “1 mol of oxygen” is ambiguous. We should refer instead to “1 mol of O_2 ” if there are N_0 oxygen *molecules*, and “1 mol of O” if there are N_0 oxygen *atoms*.

The mass of one mole of atoms of an element—the **molar mass**, with units of grams per mole—is numerically equal to the dimensionless relative atomic mass of that element, and the same relationship holds between the molar mass of a compound and its relative molecular mass. Thus, the relative molecular mass of water is 18.0152, and its molar mass is $18.0152 \text{ g mol}^{-1}$.

To determine the chemical amount, in moles, of a given substance, we use the chemist’s most powerful tool, the laboratory balance. If a sample of iron weighs 8.232 g, then

$$\begin{aligned} \text{chemical amount of iron} &= \frac{\text{number of grams of iron}}{\text{molar mass of iron}} \\ &= \frac{8.232 \text{ g Fe}}{55.847 \text{ g mol}^{-1}} \\ &= 0.1474 \text{ mol Fe} \end{aligned}$$

where the molar mass of iron was obtained from a table of relative atomic masses. The calculation can be turned around, as well. Suppose a certain chemical amount, 0.2000 mol, of water is needed in a chemical reaction. We have

$$\begin{aligned} (\text{chemical amount of water}) \times (\text{molar mass of water}) &= \text{mass of water} \\ (0.2000 \text{ mol H}_2\text{O}) \times (18.015 \text{ g mol}^{-1}) &= 3.603 \text{ g H}_2\text{O} \end{aligned}$$

FIGURE 1.13 One-mole quantities of several substances. Clockwise from top: graphite (C), potassium permanganate (KMnO_4), copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), copper (Cu), sodium chloride (NaCl), and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). Antimony (Sb) is at the center. (Leon Lewandowski)



Thus, we simply measure out 3.603 g of water. In both cases, the molar mass is the conversion factor between the substance's mass and its chemical amount in moles.

Although numbers of moles are frequently determined by weighing, it is still preferable to think of a mole as a fixed number of particles (Avogadro's number) rather than as a fixed mass. The term "mole" is thus analogous to a term such as "dozen": one dozen pennies weighs 26 g, substantially less than the mass of one dozen nickels, 60 g; but each group contains 12 coins. Figure 1.13 shows mole quantities of several substances.

EXAMPLE 1.5

Nitrogen dioxide (NO_2) is a major component of urban air pollution. For a sample containing 4.000 g of NO_2 , calculate (a) the chemical amount (the number of moles) of NO_2 and (b) the number of molecules of NO_2 .

Solution

(a) From the tabulated molar masses of nitrogen ($14.007 \text{ g mol}^{-1}$) and oxygen ($15.999 \text{ g mol}^{-1}$), the molar mass of NO_2 is

$$14.007 \text{ g mol}^{-1} + (2 \times 15.999 \text{ g mol}^{-1}) = 46.005 \text{ g mol}^{-1}$$

The chemical amount of NO_2 is then

$$\text{moles NO}_2 = \frac{4.000 \text{ g NO}_2}{46.005 \text{ g mol}^{-1}} = 0.08695 \text{ mol NO}_2$$

(b) To convert from moles to number of molecules, multiply by Avogadro's number:

$$\begin{aligned} \text{molecules NO}_2 &= (0.08695 \text{ mol NO}_2) \times 6.0221 \times 10^{23} \text{ mol}^{-1} \\ &= 5.236 \times 10^{22} \text{ molecules NO}_2 \end{aligned}$$

Related Problems: 33, 34

Density and Molecular Size

The **density** of a sample is the ratio of its mass to its volume:

$$\text{density} = \frac{\text{mass}}{\text{volume}} \quad [1.2]$$

The base unit of mass in the International System of Units (discussed in Appendix B) is the kilogram (kg), but this is often inconveniently large for practical purposes in chemistry. Frequently the gram is used instead; moreover, the gram is the standard unit for expressing molar masses. Several units for volume are in frequent use. The base SI unit of the cubic meter (m^3) is also quite unwieldy for laboratory purposes (1 m^3 of water weighs 1000 kg, or 1 metric ton). For volume we will therefore use the liter ($1 \text{ L} = 10^{-3} \text{ m}^3$) and the cubic centimeter, which is identical to the milliliter ($1 \text{ cm}^3 = 1 \text{ mL} = 10^{-3} \text{ L} = 10^{-6} \text{ m}^3$). Table 1.1 lists the densities of some substances in units of grams per cubic centimeter.

The density of a substance is not a fixed, invariant quantity but depends on the pressure and temperature at the time of measurement. For some substances (especially gases and liquids), the volume may be more convenient to measure than the mass, and when the density is known, it provides the conversion factor between volume and mass. For example, near room temperature liquid benzene (C_6H_6) has a density of 0.8765 g cm^{-3} . Suppose that 0.2124 L of benzene is measured into a container. The mass of benzene is then the product of volume and density:

$$0.2124 \text{ L} \times (1 \times 10^3 \text{ cm}^3 \text{ L}^{-1}) \times (0.8765 \text{ g cm}^{-3}) = 186.2 \text{ g}$$

Dividing this by the molar mass of benzene ($78.114 \text{ g mol}^{-1}$) gives the corresponding chemical amount, 2.384 mol .

Knowing the density and molar mass of a substance, we readily compute its **molar volume**, the volume occupied by one mole of substance:

$$V_m = \frac{\text{molar mass (g mol}^{-1}\text{)}}{\text{density (g cm}^{-3}\text{)}} = \text{molar volume (cm}^3 \text{ mol}^{-1}\text{)}$$

Near 0°C , for example, ice has a density of 0.92 g cm^{-3} , so the molar volume of solid water under these conditions is

$$V_m = \frac{18.0 \text{ g mol}^{-1}}{0.92 \text{ g cm}^{-3}} = 20 \text{ cm}^3 \text{ mol}^{-1}$$

The molar volume of a gas is much larger than this. For O_2 at room conditions, the data in Table 1.1 give a molar volume of $24,600 \text{ cm}^3 \text{ mol}^{-1} = 24.6 \text{ L mol}^{-1}$, which is more than 1000 times larger than the molar volume just computed for ice under the same conditions of temperature and pressure. How can we interpret this fact on a microscopic level? We note also that the volumes of liquids and solids do not shift very much with changes in temperature or pressure, but gas volumes are quite sensitive to these changes. A hypothesis to explain such observations is that molecules in liquids and solids are close enough to touch one another, but in a gas they are separated by large distances. If this hypothesis is correct (and it has been borne out by further study), then the sizes of the molecules themselves can be estimated from the volume per molecule in the liquid or solid state. The volume per molecule is the molar volume divided by Avogadro's number; for ice this gives

$$\text{volume per H}_2\text{O molecule} = \frac{20 \text{ cm}^3 \text{ mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 3.3 \times 10^{-23} \text{ cm}^3$$

TABLE 1.1

Densities of Some Substances[†]

Substance	Density (g cm^{-3})
Hydrogen	0.000082
Oxygen	0.00130
Water	1.00
Magnesium	1.74
Sodium chloride	2.16
Quartz	2.65
Aluminum	2.70
Iron	7.86
Copper	8.96
Silver	10.5
Lead	11.4
Mercury	13.5
Gold	19.3
Platinum	21.4

[†] These densities were measured at room temperature and at average atmospheric pressure near sea level.

FIGURE 3.13 The total dipole moment of a molecule is obtained by vector addition of its bond dipoles. This operation is performed by placing the arrows head to tail. (a) CO_2 . (b) OCS . (c) H_2O . (d) CCl_4 .

3.7

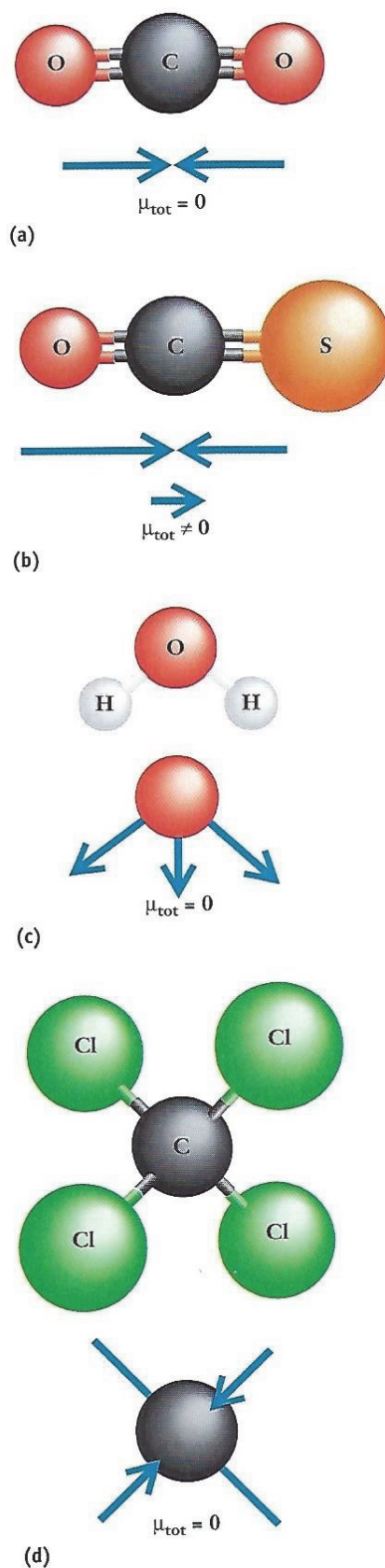
INORGANIC NOMENCLATURE AND OXIDATION NUMBERS

In Sections 3.2 and 3.4 we used the periodic table and the Lewis model to describe the transfer and sharing of electrons in chemical compounds. We conclude this chapter by discussing the systematic nomenclature of inorganic compounds. In Section 3.2, ionic compounds were named by following the name of the positive ion with the name of the negative ion. If a metal atom can form more than one stable ion, the ionic charge is given by a Roman numeral enclosed in parentheses; for example, iron(III) represents the Fe^{3+} ion. This Roman numeral notation can be generalized to apply to compounds with covalent character as well, giving rise to a quantity called *oxidation number*. Oxidation numbers are used in naming compounds, in classifying types of reactions, and in exploring the systematic chemistry of the elements.

Oxidation Number

The terms “ionic” and “covalent” have been used up to now as though they represent the complete transfer of one or more electrons from one atom to another or the equal sharing of pairs of electrons between atoms in a molecule. In actuality, both types of bonding are idealizations that rarely apply exactly. To account for the transfer of electrons from one molecule or ion to another in oxidation–reduction reactions and to name different binary compounds of the same elements, it is not necessary to have detailed knowledge of the exact electron distributions in molecules, whether they are chiefly ionic or covalent. We can assign convenient fictitious charges to the atoms in a molecule and call them **oxidation numbers**, making certain the law of charge conservation is strictly observed. Oxidation numbers are chosen so that in ionic compounds the oxidation number coincides with the charge on the ion. The following simple conventions are useful:

1. The oxidation numbers of the atoms in a neutral molecule must add up to zero, and those in an ion must add up to the charge on the ion.
2. Alkali metal atoms have oxidation number +1, alkaline earth atoms +2, in their compounds.
3. Fluorine always has oxidation number –1 in its compounds. The other halogens have oxidation number –1 in their compounds except those with oxygen and with other halogens, where they can have positive oxidation numbers.
4. Hydrogen is assigned oxidation number +1 in its compounds except in metal hydrides such as LiH , where convention 2 takes precedence and hydrogen has oxidation number –1.
5. Oxygen is assigned oxidation number –2 in compounds. There are two exceptions: in compounds with fluorine, convention 3 takes precedence, and in compounds



that contain O—O bonds, conventions 2 and 4 take precedence. Thus, the oxidation number of oxygen in OF_2 is +2; in peroxides (such as H_2O_2 and Na_2O_2) it is -1. In superoxides (such as KO_2) oxygen's oxidation number is $-\frac{1}{2}$.

Convention 1 is fundamental because it guarantees charge conservation: the total number of electrons must remain constant in chemical reactions. This rule also makes the oxidation numbers of the neutral atoms of elements all zero. Conventions 2 to 5 are based on the principle that in ionic compounds the oxidation number should equal the charge on the ion. Note that fractional oxidation numbers, though not common, are allowed and in fact necessary to be consistent with this set of conventions.

With the preceding conventions in hand, chemists can assign oxidation numbers to the atoms in the vast majority of compounds. Apply conventions 2 through 5 as listed above, noting the exceptions given; then assign oxidation numbers to the other elements in such a way that convention 1 is always obeyed. Note that convention 1 applies not only to free ions but to the components that make up ionic solids. Chlorine has oxidation number -1 not only as a free Cl^- ion but in the ionic solid AgCl and in covalent CH_3Cl . It is important to recognize common ionic species (especially molecular ions) and to know the total charges they carry. Table 3.1 listed the names and formulas of many common anions. Inspection of the table reveals that several elements exhibit different oxidation numbers in different compounds. In Ag_2S sulfur appears as the sulfide ion and has oxidation number -2, but in Ag_2SO_4 it appears as part of a sulfate (SO_4^{2-}) ion. In this case,

$$(\text{oxidation number of S}) + [4 \times (\text{oxidation number of O})] = \text{total charge on ion}$$

$$x + [4(-2)] = -2$$

$$\text{oxidation number of S} = x = +6$$

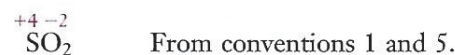
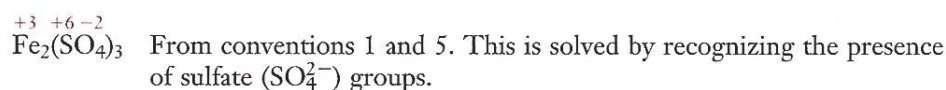
A convenient way to indicate the oxidation number of an atom is to write it directly above the corresponding symbol in the formula of the compound:



EXAMPLE 3.11

Assign oxidation numbers to the atoms in the following chemical compounds and ions: NaCl , ClO^- , $\text{Fe}_2(\text{SO}_4)_3$, SO_2 , I_2 , KMnO_4 , CaH_2 .

Solution



- I_2 From convention 1. I_2 is an element.
- $\overset{+1}{\text{K}}\overset{+7}{\text{Mn}}\overset{-2}{\text{O}_4}$ From conventions 1, 2, and 5.
- $\overset{+2}{\text{Ca}}\overset{-1}{\text{H}_2}$ From conventions 1 and 2 (metal hydride case).

Related Problems: 53, 54

Oxidation numbers must not be confused with the formal charges on Lewis dot diagrams described in Section 3.4. They resemble formal charges to the extent that both are assigned, by arbitrary conventions, to symbols in formulas for specific purposes. The purposes differ, however. Formal charges are used solely to identify preferred Lewis diagrams. Oxidation numbers are used in nomenclature, in identifying oxidation–reduction reactions, and in exploring trends in chemical reactivity across the periodic table. Oxidation numbers are often not the same as the true charges on atoms. In KMnO_4 or Mn_2O_7 , for example, Mn has the oxidation number $+7$, but the actual net charge on the atom is much less than this. A high oxidation state usually indicates significant covalent character in the bonding of that compound. The oxides of manganese with lower oxidation states (Fig. 3.14) have more ionic character.

Figure 3.15 shows the most common oxidation states of the elements of the main groups. The strong diagonal lines for these elements reflect the stability of closed electron octets. For example, the oxidation states $+6$ and -2 for sulfur would correspond to losing or gaining enough electrons to attain a noble-gas octet. The octet-based Lewis model is not useful for compounds of the transition elements, which are discussed further in Chapter 18.

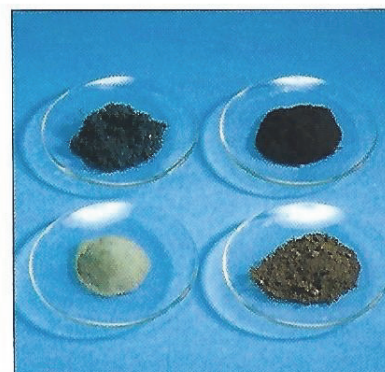


FIGURE 3.14 Several oxides of manganese. They are arranged in order of increasing oxidation number of the Mn, counterclockwise from bottom left: MnO , Mn_3O_4 , Mn_2O_3 , and MnO_2 . A compound of still higher oxidation state, Mn_2O_7 , is a dark red liquid that explodes easily. (Leon Lewandowski)

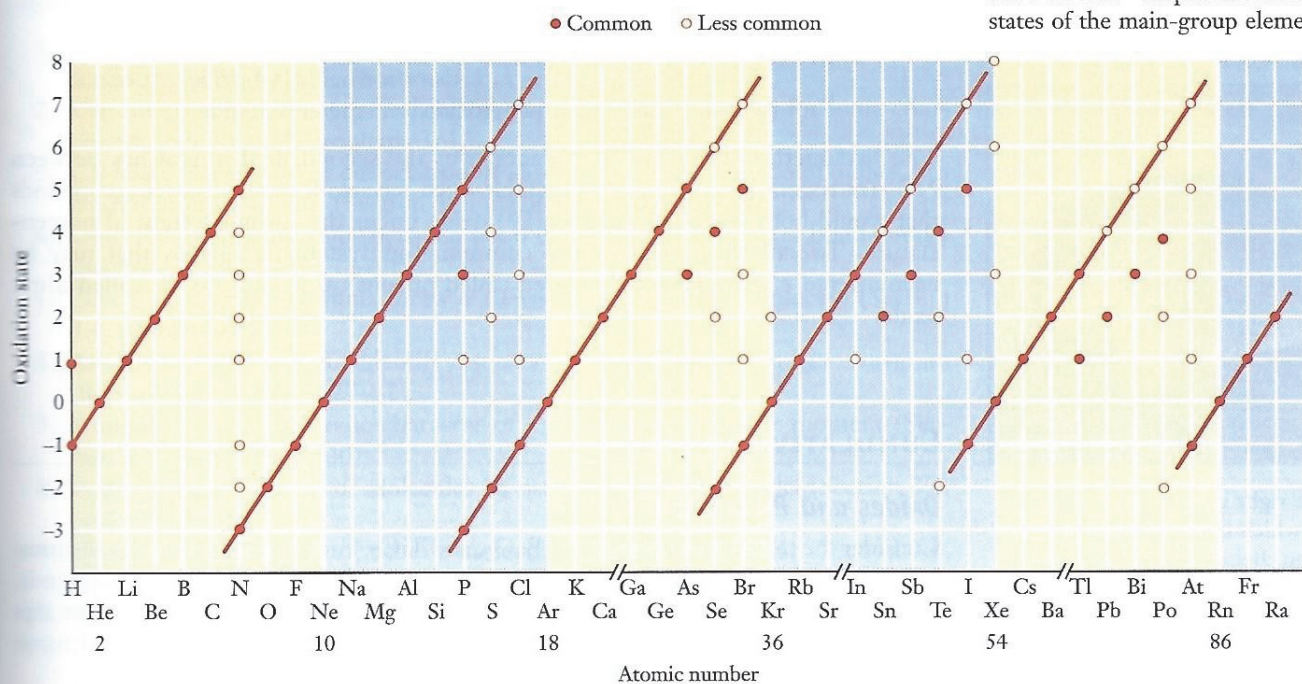


FIGURE 3.15 Important oxidation states of the main-group elements.

TABLE 3.7

Prefixes Used for Naming Binary Covalent Compounds

Number	Prefix
1	mono-
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

Naming Binary Covalent Compounds

How do we name nonionic (covalent) compounds? If a pair of elements forms only one compound, begin with the name of the element appearing first in the chemical formula, followed by the second element with the suffix *-ide* added to its root. This is quite analogous to the naming of ionic compounds. Just as NaBr is sodium bromide, so the following names designate typical covalent compounds:

HBr	hydrogen bromide	H ₂ S	hydrogen sulfide
BeCl ₂	beryllium chloride	BN	boron nitride

A number of well-established nonsystematic names continue to be used (even the strictest chemist does not call water "hydrogen oxide"!) They include

H ₂ O	water	PH ₃	phosphine
NH ₃	ammonia	AsH ₃	arsine
N ₂ H ₄	hydrazine	COCl ₂	phosgene

If a pair of elements forms more than one compound, two methods can be used to distinguish between them.

1. Use Greek prefixes (Table 3.7) to specify the number of atoms of each element in the molecular formula of the compound (*di-* for two, *tri-* for three, and so forth). If the compound is a solid without well-defined molecules, name the empirical formula in this way. The prefix for one (*mono-*) is omitted except in the case of carbon monoxide.
2. Write the oxidation number of the first-named element in Roman numerals and place it in parentheses after the name of that element.

Applying the two methods to the oxides of nitrogen gives

N ₂ O	dinitrogen oxide	nitrogen(I) oxide
NO	nitrogen oxide	nitrogen(II) oxide
N ₂ O ₃	dinitrogen trioxide	nitrogen(III) oxide
NO ₂	nitrogen dioxide	nitrogen(IV) oxide
N ₂ O ₄	dinitrogen tetraoxide	nitrogen(IV) oxide
N ₂ O ₅	dinitrogen pentaoxide	nitrogen(V) oxide

The first method has some advantages over the second. It distinguishes between NO₂ (nitrogen dioxide) and N₂O₄ (dinitrogen tetraoxide), two distinct compounds that would both be called nitrogen(IV) oxide under the second system of nomenclature. Two of these oxides have common (nonsystematic) names that may be encountered elsewhere: N₂O is often called nitrous oxide, and NO is called nitric oxide.



On the right is a sample of rutile, TiO₂, which is the primary ore of titanium. Behind it is a large quartz crystal through which slender rutile hairs penetrate. Crystals of this type are called Venus hairstone. (Michael Dalton/Fundamental Photographs)

CUMULATIVE EXERCISE

Oxides and Peroxides

Consider the three compounds KO₂, BaO₂, and TiO₂. Each contains two oxygen atoms per metal atom, but the oxygen occurs in different forms in the three compounds.

(a) The oxygen in TiO₂ occurs as O²⁻ ions. Give the Lewis dot symbol for this ion. How many valence electrons does this ion have? What is the chemical name for TiO₂?

(b) Recall that Group II elements form stable +2 ions. By referring to Table 3.1, identify the oxygen-containing ion in BaO_2 and give the name of the compound. Draw a Lewis diagram for the oxygen-containing ion, showing formal charge. Is the bond in this ion a single or a double bond?

(c) Recall that Group I elements form stable +1 ions. By referring to Table 3.1, identify the oxygen-containing ion in KO_2 and give the name of the compound. Show that the oxygen-containing ion is an odd-electron species. Draw the best Lewis diagram you can for it.

Answers

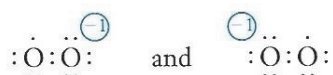
(a) The ion $:\ddot{\text{O}}:^{2-}$ has eight valence electrons (an octet). TiO_2 is titanium(IV) oxide.

(b) The ion in BaO_2 must be the peroxide ion (O_2^{2-}), and the compound is barium peroxide. The Lewis diagram for the peroxide ion is



and the O—O bond is a single bond.

(c) The ion in KO_2 must be the superoxide ion (O_2^-), and the compound is potassium superoxide. The superoxide ion has 13 valence electrons. The best Lewis diagram is a pair of resonance diagrams



in which only one of the oxygen atoms attains an octet electron configuration.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to

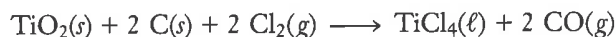
1. Describe the trends in ionization energy, electron affinity, and electronegativity across the periodic table (Section 3.1).
2. Use the principle of charge balance to write chemical formulas for ionic compounds (Section 3.2, problems 3–10).
3. Calculate the energy of dissociation of gaseous diatomic ionic compounds into neutral atoms and ions (Section 3.2, problems 11–12).
4. Describe the relationships between bond order, bond length, and bond energy (Section 3.3, problems 13–14).
5. Given a molecular formula, draw a Lewis diagram for the molecule (Section 3.4, problems 21–24).
6. Assign formal charges and identify resonance diagrams for a given Lewis diagram (Section 3.4, problems 27–32).
7. Estimate the percent ionic character of a bond from its dipole moment (Section 3.5, problems 37–40).
8. Predict the geometries of molecules by use of the VSEPR model (Section 3.6, problems 41–46).
9. Determine whether a polyatomic molecule is polar or nonpolar (Section 3.6, problems 47–48).
10. Assign oxidation numbers to atoms in compounds (Section 3.7, problems 53–54).
11. Name inorganic compounds, given their chemical formulas, and write chemical formulas for named inorganic compounds (Section 3.7, problems 55–58).

demand for these two products is rarely in ideal balance, the prices of both commodities fluctuate. A byproduct of the reaction is hydrogen. It can react directly with chlorine to give gaseous hydrogen chloride of high purity, although there are less expensive sources for this chemical. Alternatively, the chlor-alkali process can be coupled with a fertilizer plant, and the hydrogen can be reacted with nitrogen to make ammonia (see Section 21.3).

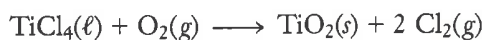
22.2

THE CHEMISTRY OF CHLORINE, BROMINE, AND IODINE

Chlorine, bromine, and iodine resemble one another much more closely than they do fluorine, whose special properties are discussed in Section 22.3. Section 22.1 described the production of chlorine and its role in making bleaches. That role is now overshadowed by the importance of chlorine in the manufacture of chlorinated hydrocarbons for use as solvents, pesticides, and plastics such as polyvinyl chloride (Sec. 23.3). Growing concern about the environmental effects and toxic properties of chlorinated hydrocarbons (see Fig. 22.5) has slowed the growth of the industry. Another major use for chlorine is the purification of titanium dioxide. This substance occurs in impure form; it reacts above 900°C with chlorine and coke to give titanium tetrachloride:



Because TiCl_4 is a volatile liquid (b.p. 136°C), it can easily be purified by distillation and then oxidized to pure titanium dioxide, regenerating chlorine:



Titanium dioxide is the major white pigment used in paint. It is more opaque than other pigments, and so paints containing it have high covering power.

Bromine is obtained largely from naturally occurring brines, where it occurs as aqueous bromide ion (Br^-). Treatment of these brines with chlorine (Fig. 22.6) results in the reaction



This equilibrium lies to the right because chlorine is a stronger oxidizing agent than bromine. The bromine liberated is swept out with steam, distilled, and purified. Until recently, the most important use for bromine was in the production of dibro-

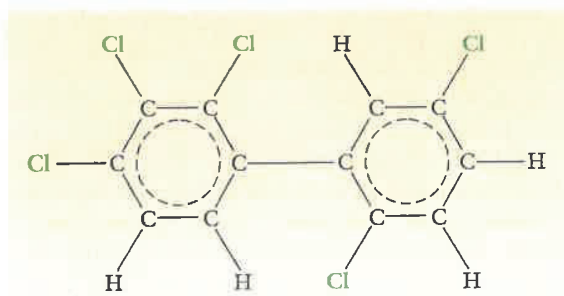


FIGURE 22.5 One of the many polychlorinated biphenyls (PCBs), which were once used as insulating fluids in electrical transformers. These compounds are being phased out because of their toxic effect on marine life.

moethane ($\text{C}_2\text{H}_4\text{Br}_2$), which was used in gasoline to scavenge the lead deposited from the breakdown of tetraethyl lead; the use of this "antiknock" additive is decreasing, however, because of concerns about contamination of the environment with lead. A major current use for bromine is in the production of flame-retardant organic compounds. Aqueous solutions of CaBr_2 and ZnBr_2 are also employed as high-density fluids to recover oil from deep wells.

Iodine occurs in seawater to the extent of only $6 \times 10^{-7}\%$, but it is concentrated in certain species of kelp, from whose ash its recovery is commercially feasible. Iodine is present in the growth-regulating hormone thyroxine, produced by the thyroid gland. Much of the table salt sold has 0.01% NaI added to prevent goiter, the enlargement of the thyroid gland. Silver iodide is used in high-speed photographic film, whereas silver bromide and silver chloride are used in slower speed film and in photographic printing paper.

The hydrogen halides HCl , HBr , and HI are all gases at room conditions, and all three dissolve in water to form strong acids. Hydrogen chloride is usually prepared by the direct combination of hydrogen and chlorine over a platinum catalyst or as a byproduct of organic chemicals processing. Its aqueous solution, hydrochloric acid, is a major industrial acid, used extensively for the cleaning of metal surfaces. Hydrogen bromide and hydrogen iodide have fewer uses. Their aqueous solutions are prepared on a laboratory scale by the hydrolysis of phosphorus tribromide or phosphorus triiodide:

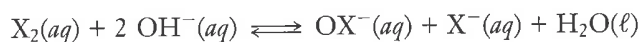


Solution Chemistry of the Halogens

When chlorine, bromine, or iodine is added to water, the halogen disproportionates in part to form its halo- and hypohalous acids according to the equilibrium



The equilibrium constant for this reaction is very small, but the reaction can be shifted to the right in basic solution, where HOX is neutralized and the overall reaction is



No complications arise with chlorine, and stable solutions of chloride and hypochlorite ions result at 25°C . In this way, a solution of sodium hypochlorite (NaOCl)—used as a laundry bleach—can be prepared. The hypochlorite ion is thermodynamically unstable with respect to disproportionation into chloride and chlorate ions,



but at ordinary temperatures this reaction is very slow. When the temperature is increased to about 75°C , however, the rate of disproportionation is rapid.

The equilibrium constant for the disproportionation of bromine in water to bromide and hypobromite ions is even smaller than that for the disproportionation of chlorine; if the concentration of base is increased, the further disproportionation of hypobromite to bromide and bromate ions occurs rapidly even at 25°C . The same is true of iodine, but to an even greater extent. The solubility of iodine in water at 25°C is only $1.34 \times 10^{-3} \text{ M}$, but in the presence of iodide ion, much more dissolves as triiodide ion forms:

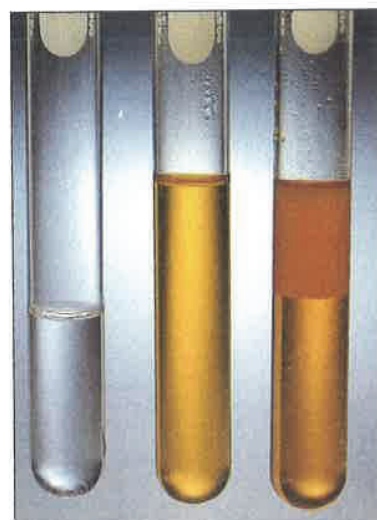
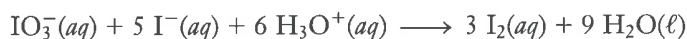


FIGURE 22.6 Bromide ion (left) is colorless. Oxidation by chlorine yields bromine (center), which is colored in aqueous solution. The color is even more intense in an organic solvent (upper layer on right). (Charles D. Winters)

The I_3^- ion has a linear structure that is symmetric in solution and in certain crystalline salts but unsymmetric (unequal I—I distances) in others.

Among the possible acids of formula HXO_3 , only iodic acid exists in anhydrous form, a crystalline solid that is stable up to its melting point. The alkali chlorates, bromates, and iodates have the generic formula MXO_3 , and all are well-characterized salts that can be crystallized from aqueous solution. Acidic solutions of the salts are powerful oxidizing agents that react quantitatively with their corresponding halide ions to yield the halogen:



When potassium chlorate is carefully heated in the absence of catalysts, it is converted to potassium perchlorate:



Perchloric acid can be formed by heating potassium perchlorate with concentrated sulfuric acid, but this is a somewhat hazardous reaction that is prone to explosions. A safer procedure is to oxidize an aqueous solution of an alkali chlorate at the anode of an electrolytic cell:

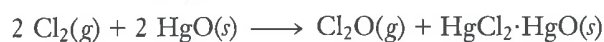


Perchloric acid is a colorless liquid that boils at 82°C . In its anhydrous form it is a powerful oxidizing agent, but in aqueous solution at moderate concentration it does not display oxidizing ability. Aqueous perbromic acid, on the other hand, is a powerful oxidizing agent that is also formed electrolytically.

Aqueous periodic acid is a more useful oxidizing agent than either perbromic or perchloric acid, because its behavior is more controllable. Periodic acid exists in several forms, the simplest of which is metaperiodic acid (HIO_4). Like iodic acid, metaperiodic acid is a crystalline solid at room temperature. It is possible to expand the coordination sphere of iodine(VII) from four to six ligands by the addition of two water molecules, and the resulting orthoperiodic acid has the formula H_5IO_6 . This substance is a crystalline solid that decomposes at 140°C .

Halogen Oxides

Chlorine, bromine, and iodine form several oxides, most of which are rather unstable. Dichlorine monoxide is prepared by reaction of chlorine with mercury(II) oxide:



In basic solution it forms hypochlorites, as it is the anhydride of hypochlorous acid:



Chlorine dioxide is a very unstable gas that is prepared by reaction of chlorine with silver chlorate:



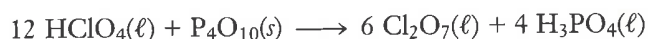
It is a very powerful oxidizing agent that is used to bleach wheat flour. Like nitrogen dioxide, it consists of "odd-electron" molecules, but unlike that molecule, it shows little tendency to dimerize. In basic solution it disproportionates to form chlorite and chlorate ions and can be regarded as a mixed anhydride of chlorous and chloric acids:



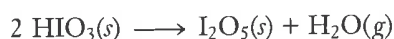


FIGURE 22.7 Iodine reacts with starch to form a dark-colored complex. (*Leon Lewandowski*)

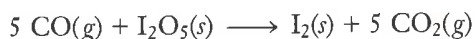
The most stable of the chlorine oxides is dichlorine heptaoxide (Cl_2O_7), a colorless liquid that boils without decomposing at 82°C . It is prepared by dehydration of perchloric acid with P_4O_{10} :



The oxides of bromine, Br_2O and BrO_2 , are prepared by methods that parallel those for the corresponding oxides of chlorine. The most important of the iodine oxides is diiodine pentaoxide, a white crystalline solid that is prepared by thermally dehydrating iodic acid:



Diiodine pentaoxide is useful in analytical chemistry for the detection and quantitative determination of carbon monoxide, which it readily oxidizes:



The iodine released in this reaction is detected visually by means of the deep blue-black colored complex it forms with starch (Fig. 22.7).

22.3

FLUORINE AND ITS COMPOUNDS

Fluorine ranks 13th in abundance among the elements in the rocks of the earth's crust, and its compounds were used as early as 1670 for the decorative etching of glass. Yet heroic efforts to isolate it as a free element failed for many years, until 1886. The difficulty of preparing elemental fluorine results from the fact that it is among the strongest oxidizing agents. The other halogens are moderate to very good at accepting electrons in aqueous media, as shown by their standard reduction potentials, 0.535 V (for I_2), 1.065 V (for Br_2), and 1.358 V (for Cl_2). Fluorine is *avid* for electrons:



Because fluorine is so good at gaining electrons, fluorides strongly resist oxidation.

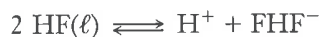
The major source of fluorine is the ore fluor spar, which contains fluorite (CaF_2) (Fig. 19.30). Figure 19.19b showed the cubic structure of CaF_2 . Another source of fluorine is fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, which is mined in great quantity to make phosphate fertilizer (Section 21.2). At one time, fluorine-containing byproducts (HF , SiF_4 , and H_2SiF_6) from fertilizer plants were valueless and created environmental pollution comparable to the hydrogen chloride pollution caused by the Leblanc process (Section 22.1). Now the fluorine from fluorapatite has economic value in making fluorine compounds.

Hydrogen Fluoride

Almost half of the fluor spar that is mined is used in steelmaking to increase the fluidity of the slag. Most of the remainder is reacted with concentrated sulfuric acid to make hydrogen fluoride:



The resulting gaseous HF is condensed and redistilled to free it from sulfur oxides. Anhydrous hydrogen fluoride is a colorless liquid that freezes at -83.37°C and boils at 19.54°C , near room temperature. The boiling point far exceeds what the trend among the other hydrogen halides predicts and is strong evidence for association of the HF molecules (by hydrogen bonds) in the liquid. In this and other physical properties, HF is closer to water and ammonia than to HCl, HBr, or HI. As pure liquids, both water and hydrogen fluoride contain polar molecules but few ions; both are poor electrical conductors. Liquid hydrogen fluoride undergoes autoionization much as water does:



The reaction has an equilibrium constant (at 19.5°C) of 2.0×10^{-14} , a value close to the room-temperature autoionization constant of water (1.0×10^{-14}).

Hydrogen fluoride in aqueous solution is a weak acid ($K_a = 6.6 \times 10^{-4}$ at 25°C), quite unlike HCl, HBr, and HI, which are strong acids. Its weakness as an acid is due both to the strength of the H—F bond and to the extensive hydrogen bonding in its aqueous solutions. Fluoride ions interact so strongly with hydronium ions, H_3O^+ , that they remain bound in $\text{F}^- \cdots \text{H}_3\text{O}^+$ complexes rather than separating as chloride, bromide, and iodide ions do.

Anhydrous hydrogen fluoride is quite poisonous, causes serious burns, and corrodes silicate glass by the reaction



This reaction underlies one long-standing use of aqueous hydrogen fluoride: etching decorative patterns in glass (Fig. 22.8). Hydrogen fluoride does not attack Teflon and certain other fluorine-containing plastics. Their availability in recent years has made it easier to handle hydrogen fluoride safely. Another major use of $\text{HF}(g)$ is in the aluminum industry. It reacts with $\text{NaAlO}_2(aq)$, itself prepared from bauxite ore ($\text{Al}_2\text{O}_3(s)$) and $\text{NaOH}(aq)$, to make synthetic cryolite according to the equation



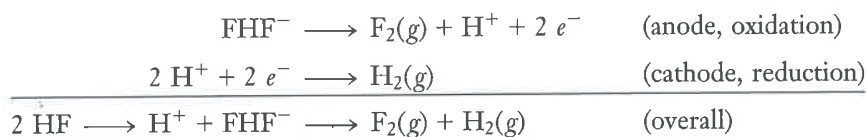
The very important Hall–Héroult process to produce aluminum (Fig. 20.16) depends on the electrolysis of solutions of Al_2O_3 in molten cryolite.



FIGURE 22.8 Glass can be etched in intricate patterns with aqueous hydrogen fluoride. The geometric patterns and background were formed by protecting portions of the glass and exposing the unprotected areas to $\text{HF}(aq)$. (Copyright Christie's Images)

The Preparation of Fluorine

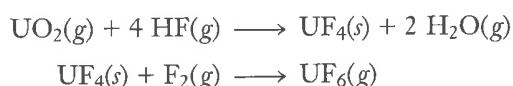
Elemental fluorine is produced from hydrogen fluoride by a method similar to that first used by Moissan—the electrolysis of molten potassium hydrogen fluoride ($\text{KF} \cdot 2\text{HF}$), a solution of KF in liquid HF . In the solution, F^- ion associates strongly with HF to form FHF^- (the hydrogen difluoride ion), the species that actually loses the electrons:



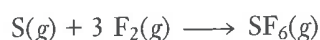
This process resembles the electrolytic production of $\text{Cl}_2(\text{g})$ (Section 22.1). As fluorine and hydrogen evolve, $\text{HF}(\text{g})$ is fed in continuously to keep the electrolyte composition constant at $\text{KF} \cdot 2\text{HF}$. A commercial fluorine cell uses a steel cathode and carbon anode. The cells are carefully engineered to prevent contact between the product gases, which react at catastrophic speed.

Fluorine is a very pale yellow gas. It condenses to a canary-yellow liquid at -188.14°C and solidifies at -219.62°C . It is an exceedingly toxic substance. Concentrations exceeding 25 ppm in air quickly damage the eyes, nose, lungs, and skin. Fluorine's pungent, irritating odor makes it first detectable in air at a concentration of about 3 ppm, well below the level of acute poisoning but above the recommended safe working level of 0.1 ppm. The ferocious reactivity of fluorine demands the utmost care in its use, and handling procedures that minimize the hazards have been developed. Certain metals (nickel, copper, steel, and the nickel-copper alloy Monel metal) resist attack by fluorine by forming a layer of a fluoride salt on their surfaces. Reactions can be carried out at room temperature in vessels made of these metals. The pure element is regularly packaged and shipped as a compressed gas in special cylinders, but it is also often generated at the point of use.

The role of elemental fluorine in the chemical industry has grown to major proportions since 1945. Before then, elemental fluorine was mostly a laboratory curiosity. The motive for finding ways to prepare, purify, and handle it was the need to synthesize a volatile uranium compound that could separate the ^{235}U and ^{238}U isotopes by gaseous diffusion, as described in Section 4.6. Uranium hexafluoride met that requirement, and gaseous diffusion is still used for preparing ^{235}U -enriched reactor fuel. At present, more than half of the world's production of $\text{F}_2(\text{g})$ is used to make UF_6 from uranium(IV) oxide by these reactions:



Most of the remaining fluorine production goes to make sulfur hexafluoride by the reaction



This unreactive gas is a good electrical insulator. Its presence within heavy-duty electrical switches minimizes arcing or sparking when the switches are thrown. Electrical discharges that do occur in an SF_6 atmosphere decompose the gas to an extent (into sulfur and fluorine), but the dissociation products rapidly recombine. Some triple-pane windows are manufactured with SF_6 sealed in the "dead-air" spaces between the panes because it cuts heat transmission and muffles sound better than air.

Fluorine and the Other Halogens

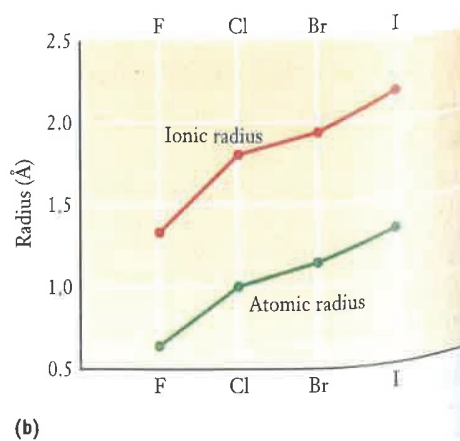
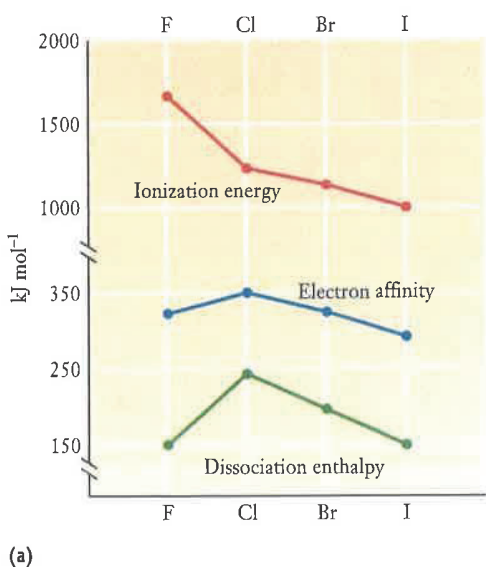
The differences between fluorine and the other halogens are extreme enough to place fluorine in a class by itself. It is much more reactive *than* chlorine, bromine, and iodine; indeed, it is by far the most reactive of all the *elements*. In forming a compound, a fluorine atom either shares electrons in a single covalent bond or gains one electron to form the fluoride ion (F^-). In either case, it always attains a noble-gas electron configuration ($1s^2 2s^2 2p^6$). The other halogens tend to behave similarly but tolerate numerous exceptions; fluorine does not. The rules for assigning oxidation numbers (Section 3.7) recognize the special character of fluorine by setting its oxidation number in compounds always equal to -1 . Chlorine, bromine, and iodine may have positive oxidation numbers.

The chemical and physical properties of fluorine (and its compounds) deviate from the values that would be predicted by extrapolation of the trends among the other halogens. Figure 22.9 presents some data from Appendix F that show this deviation. The bond dissociation energy of F_2 is *smaller* than would be expected from the trend among the other halogens, but the first ionization energy of F is *greater*. Despite the position of F as the most electronegative of the elements, electron-affinity data show that $F(g)$ accepts another electron (to form the gaseous anion) *less* readily than $Cl(g)$ and only slightly more readily than $Br(g)$. The unexpectedly low electron affinity of a fluorine atom is related to the contracted size of the atom. As Figure 22.9b shows, $F(g)$ and $F^-(g)$ are smaller than an extrapolation of the trends among the other halogens would predict, causing crowding and greater mutual repulsion among the electrons in their $n = 2$ quantum levels.

Strong bonds, both covalent and ionic, characterize the interaction of fluorine with most other elements. Figure 22.10a shows that the $H-F$, $C-F$, and $Na-F$ bond dissociation enthalpies exceed those of H , C , and Na combined with the other halogens. Fluorine's strong bonds with other elements and weak bond with itself (in the F_2 molecule the bond dissociation enthalpy is only 158 kJ mol^{-1}) together explain its terrific reactivity. Both factors are traceable to the small size of the fluorine atom. The two atoms in the fluorine molecule are only $1.417 \text{ \AA}$ apart. This puts their lone-

FIGURE 22.9 The measured physical properties of fluorine often do not fall on the trend lines defined by the behavior of the other halogens.

(a) Here, the ionization energy of fluorine is unexpectedly high, and its electron affinity and bond dissociation enthalpy are unexpectedly low. (b) The sizes of the fluorine atom and the fluoride ion are both smaller than predicted by comparison with the other halogens.



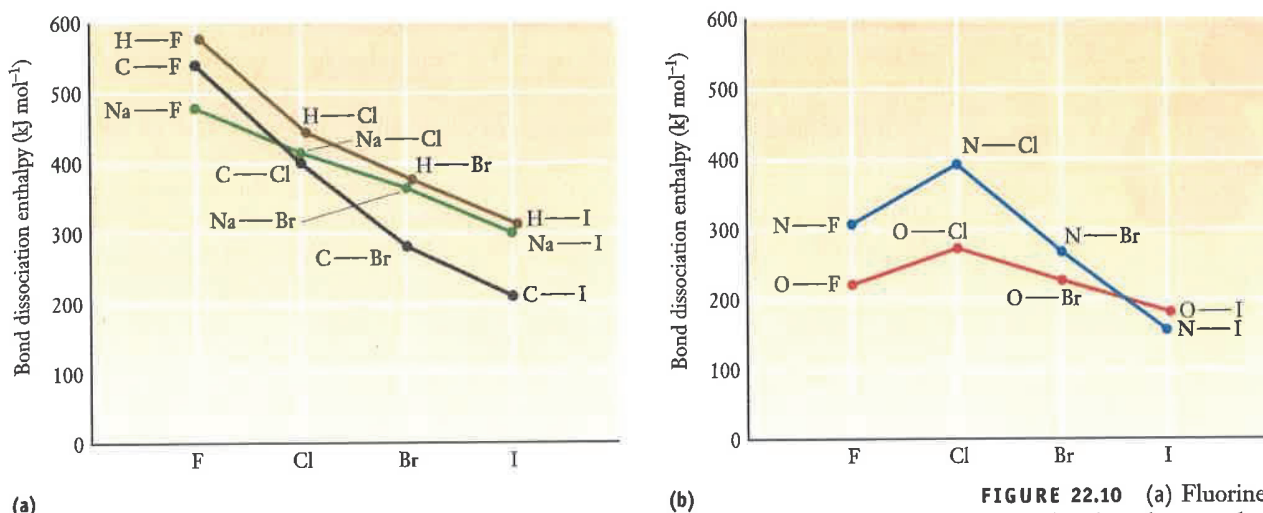


FIGURE 22.10 (a) Fluorine forms strong bonds with more electropositive elements such as C, H, and Na. (b) In contrast, fluorine forms unexpectedly weak bonds with the electronegative elements N and O in comparison to the bonds formed by the other halogens.

pair electrons closer to each other than those in the other halogens: repulsion among them lowers the bond dissociation energy. Small fluorine makes short bonds to non-fluorine atoms, as well. Lone-pair repulsion of the type just described becomes important only with elements that, like fluorine itself, are small and electronegative. Hence, O—F and N—F bonds are, like the F—F bond, weaker than would otherwise be expected (Fig. 22.10b).

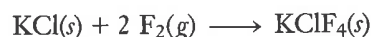
Because fluorine atoms are small, many of them fit around a given central atom before crowding each other. Therefore, atoms often attain higher coordination numbers with fluorine than with other elements. In many fluorides, such as K₂[NiF₆], Cs[AuF₆], and PtF₆, the central element has an unexpectedly high oxidation number. The other halogens offer no comparable compounds.

Reactions of Fluorine

In general, fluorine reacts with other elements and compounds by oxidizing them. It displaces the other, less reactive, halogens from compounds, just as chlorine displaces bromine and iodine, the elements located below it in the periodic table, and bromine displaces iodine. An example is the reaction



Fluorine sometimes breaks this pattern by going much further. Thus, if F₂(g) is heated with potassium chloride, the reaction is



Here the chlorine is not displaced from the compound but oxidized to the +3 state and surrounded by fluorine atoms in the “tetrafluorochlorate(III)” ion. Further heating of KClF₄(s) with F₂ eventually does displace chlorine from potassium but in an unexpected form, ClF₅(g):



In a variation, fluorine oxidizes iodine in potassium iodide and also displaces it:



Physical Properties of the Elements

Hydrogen and the Alkali Metals (Group I Elements)

	Hydrogen	Lithium	Sodium	Potassium	Rubidium	Cesium	Francium
Atomic number	1	3	11	19	37	55	87
Atomic mass	1.00794	6.941	22.98977	39.0983	85.4678	132.9054	(223)
Melting point (°C)	-259.14	180.54	97.81	63.65	38.89	28.40	25
Boiling point (°C)	-252.87	1347	903.8	774	688	678.4	677
Density at 25°C (g cm ⁻³)	0.070	0.534	0.971	0.862	1.532	1.878	
	(-253°C)						
Color	Colorless	Silver	Silver	Silver	Silver	Silver	
Ground-state electron configuration	1s ¹	[He]2s ¹	[Ne]3s ¹	[Ar]4s ¹	[Kr]5s ¹	[Xe]6s ¹	[Rn]7s ¹
Ionization energy [†]	1312.0	520.2	495.8	418.8	403.0	375.7	≈400
Electron affinity [†]	72.770	59.63	52.867	48.384	46.884	45.505	est. 44
Electronegativity	2.20	0.98	0.93	0.82	0.82	0.79	0.70
Ionic radius (Å)	1.46(H ⁻)	0.68	0.98	1.33	1.48	1.67	≈1.8
Atomic radius (Å)	0.37	1.52	1.86	2.27	2.47	2.65	≈2.7
Enthalpy of fusion [†]	0.1172	3.000	2.602	2.335	2.351	2.09	
Enthalpy of vaporization [†]	0.4522	147.1	97.42	89.6	76.9	67.8	
Bond enthalpy of M ₂ [†]	436	102.8	72.6	54.8	51.0	44.8	
Standard reduction potential (volts)	0	-3.045	-2.7109	-2.924	-2.925	-2.923	≈2.9
	H ⁺ /H ₂	Li ⁺ /Li	Na ⁺ /Na	K ⁺ /K	Rb ⁺ /Rb	Cs ⁺ /Cs	Fr ⁺ /Fr

[†] In kilojoules per mole.

The Alkaline-Earth Metals (Group II Elements)

	Beryllium	Magnesium	Calcium	Strontium	Barium	Radium
Atomic number	4	12	20	38	56	88
Atomic mass	9.01218	24.3050	40.078	87.62	137.327	(226)
Melting point (°C)	1283	648.8	839	769	725	700
Boiling point (°C)	2484	1105	1484	1384	1640	
Density at 25°C (g cm ⁻³)	1.848	1.738	1.55	2.54	3.51	5
Color	Gray	Silver	Silver	Silver	Silver-yellow	Silver
Ground-state electron configuration	[He]2s ²	[Ne]3s ²	[Ar]4s ²	[Kr]5s ²	[Xe]6s ²	[Rn]7s ²
Ionization energy [†]	899.4	737.7	589.8	549.5	502.9	509.3
Electron affinity [†]	< 0	< 0	2.0	4.6	13.95	> 0
Electronegativity	1.57	1.31	1.00	0.95	0.89	0.90
Ionic radius (Å)	0.31	0.66	0.99	1.13	1.35	1.43
Atomic radius (Å)	1.13	1.60	1.97	2.15	2.17	2.23
Enthalpy of fusion [†]	11.6	8.95	8.95	9.62	7.66	7.15
Enthalpy of vaporization [†]	297.6	127.6	154.7	154.4	150.9	136.7
Bond enthalpy of M ₂ [†]	9.46					
Standard reduction potential (volts)	-1.70	-2.375	-2.76	-2.89	-2.90	-2.916
	Be ²⁺ /Be	Mg ²⁺ /Mg	Ca ²⁺ /Ca	Sr ²⁺ /Sr	Ba ²⁺ /Ba	Ra ²⁺ /Ra

Group III Elements

	Boron	Aluminum	Gallium	Indium	Thallium
Atomic number	5	13	31	49	81
Atomic mass	10.811	26.98154	69.723	114.82	204.3833
Melting point (°C)	2300	660.37	29.78	156.61	303.5
Boiling point (°C)	3658	2467	2403	2080	1457
Density at 25°C (g cm ⁻³)	2.34	2.702	5.904	7.30	11.85
Color	Yellow	Silver	Silver	Silver	Blue-white
Ground-state electron configuration	[He]2s ² 2p ¹	[Ne]3s ² 3p ¹	[Ar]3d ¹⁰ 4s ² 4p ¹	[Kr]4d ¹⁰ 5s ² 5p ¹	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹
Ionization energy [†]	800.6	577.6	578.8	558.3	589.3
Electron affinity [†]	26.7	42.6	29	29	≈20
Electronegativity	2.04	1.61	1.81	1.78	1.83
Ionic radius (Å)	0.23 (+3)	0.51 (+3)	0.62 (+3)	0.81 (+3)	0.95 (+3)
Atomic radius (Å)	0.88	1.43	1.22	1.63	1.70
Enthalpy of fusion [†]	22.6	10.75	5.59	3.26	4.08
Enthalpy of vaporization [†]	508	291	272	243	182
Bond enthalpy of M ₂ [†]	295	167	116	106	≈63
Standard reduction potential (volts)	-0.890	-1.706	-0.560	-0.338	0.719
	B(OH) ₃ /B	Al ³⁺ /Al	Ga ³⁺ /Ga	In ³⁺ /In	Tl ³⁺ /Tl

[†] In kilojoules per mole.

Group IV Elements

	Carbon	Silicon	Germanium	Tin	Lead
Atomic number	6	14	32	50	82
Atomic mass	12.011	28.0855	72.61	118.710	207.2
Melting point (°C)	3550	1410	937.4	231.9681	327.502
Boiling point (°C)	4827	2355	2830	2270	1740
Density at 25°C (g cm ⁻³)	2.25 (gr) 3.51 (dia)	2.33	5.323	5.75 (gray) 7.31 (white)	11.35
Color	Black (gr) Colorless (dia)	Gray	Gray-white	Silver	Blue-white
Ground-state electron configuration	[He]2s ² 2p ²	[Ne]3s ² 3p ²	[Ar]3d ¹⁰ 4s ² 4p ²	[Kr]4d ¹⁰ 5s ² 5p ²	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ²
Ionization energy [†]	1086.4	786.4	762.2	708.6	715.5
Electron affinity [†]	121.85	133.6	≈120	≈120	35.1
Electronegativity	2.55	1.90	2.01	1.88	2.10
Ionic radius (Å)	0.15 (+4) 2.60 (-4)	0.42 (+4) 2.71 (-4)	0.53 (+4) 0.73 (+2) 2.72 (-4)	0.71 (+4) 0.93 (+2)	0.84 (+4) 1.20 (+2)
Atomic radius (Å)	0.77	1.17	1.22	1.40	1.75
Enthalpy of fusion [†]	105.0	50.2	34.7	6.99	4.774
Enthalpy of vaporization [†]	718.9	359	328	302	195.6
Bond enthalpy of M ₂ [†]	178	317	280	192	61
Standard reduction potential (volts)			-0.13 H ₂ GeO ₃ , H ⁺ /Ge	-0.1364 Sn ²⁺ /Sn	-0.1263 Pb ²⁺ /Pb

Group V Elements

	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Atomic number	7	15	33	51	83
Atomic mass	14.00674	30.97376	74.92159	121.75	208.9804
Melting point (°C)	-209.86	44.1	817 (28 atm.)	630.74	271.3
Boiling point (°C)	-195.8	280	613 (subl.)	1750	1560
Density at 25°C (g cm ⁻³)	0.808 (-196°C)	1.82 (white) 2.20 (red)	5.727	6.691	9.747
Color	Colorless	2.69 (black)	Gray	Blue-white	White
Ground-state electron configuration	[He]2s ² 2p ³	[Ne]3s ² 3p ³	[Ar]3d ¹⁰ 4s ² 4p ³	[Kr]4d ¹⁰ 5s ² 5p ³	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ³
Ionization energy [†]	1402.3	1011.7	947	833.7	703.3
Electron affinity [†]	-7	72.03	≈80	103	91.3
Electronegativity	3.04	2.19	2.18	2.05	2.02
Ionic radius (Å)	1.71 (-3)	0.44 (+3) 2.12 (-3)	0.46 (+5) 0.58 (+3) 2.22 (-3)	0.62 (+5) 0.76 (+3) 2.45 (-3)	0.96 (+3)
Atomic radius (Å)	0.70	1.10	1.21	1.41	1.55
Enthalpy of fusion [†]	0.720	6.587	27.72	20.91	10.88
Enthalpy of vaporization [†]	5.608	59.03	334	262.5	184.6
Bond enthalpy of M ₂ [†]	945	485	383	289	194
Standard reduction potential (volts)	0.96 NO ₃ ⁻ , H ⁺ /NO	-0.276 H ₃ PO ₄ /H ₃ PO ₃	0.234 As ₂ O ₃ , H ⁺ /As	0.1445 Sb ₂ O ₃ , H ⁺ /Sb	-0.46 Bi ₂ O ₃ , OH ⁻ /Bi

[†] In kilojoules per mole.

The Chalcogens (Group VI Elements)

	Oxygen	Sulfur	Selenium	Tellurium	Polonium
Atomic number	8	16	34	52	84
Atomic mass	15.9994	32.066	78.96	127.60	(209)
Melting point (°C)	-218.4	119.0 (mon.) 112.8 (rhomb.)	217	449.5	254
Boiling point (°C)	-182.962	444.674	684.9	989.8	962
Density at 25°C (g cm ⁻³)	1.14 (-183°C)	1.957 (mon.) 2.07 (rhomb.)	4.79	6.24	9.32
Color	Pale blue (ℓ)	Yellow	Gray	Silver	Silver-gray
Ground-state electron configuration	[He]2s ² 2p ⁴	[Ne]3s ² 3p ⁴	[Ar]3d ¹⁰ 4s ² 4p ⁴	[Kr]4d ¹⁰ 5s ² 5p ⁴	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴
Ionization energy [†]	1313.9	999.6	940.9	869.3	812
Electron affinity [†]	140.97676	200.4116	194.967	190.15	≈180
Electronegativity	3.44	2.58	2.55	2.10	2.00
Ionic radius (Å)	1.40 (-2)	0.29 (+6) 1.84 (-2)	0.42 (+6) 1.98 (-2)	0.56 (+6) 2.21 (-2)	0.67 (+6) 2.30 (-2)
Atomic radius (Å)	0.66	1.04	1.17	1.43	1.67
Enthalpy of fusion [†]	0.4187	1.411	5.443	17.50	10
Enthalpy of vaporization [†]	6.819	238	207	195	90
Bond enthalpy of M ₂ [†]	498	429	308	225	
Standard reduction potential (volts)	1.229 O ₂ /H ⁺ /H ₂ O	-0.508 S/S ²⁻	-0.78 Se/Se ²⁻	-0.92 Te/Te ²⁻	≈-1.4 Po/Po ²⁻

The Halogens (Group VII Elements)

	Fluorine	Chlorine	Bromine	Iodine	Astatine
Atomic number	9	17	35	53	85
Atomic mass	18.998403	35.4527	79.904	126.90447	(210)
Melting point (°C)	-219.62	-100.98	-7.25	113.5	302
Boiling point (°C)	-188.14	-34.6	58.78	184.35	337
Density at 25°C (g cm ⁻³)	1.108 (-189°C)	1.367 (-34.6°C)	3.119	4.93	
Color	Yellow	Yellow-green	Deep red	Violet-black	
Ground-state electron configuration	[He]2s ² 2p ⁵	[Ne]3s ² 3p ⁵	[Ar]3d ¹⁰ 4s ² 4p ⁵	[Kr]4d ¹⁰ 5s ² 5p ⁵	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵
Ionization energy [†]	1681.0	1251.1	1139.9	1008.4	≈930
Electron affinity [†]	328.0	349.0	324.7	295.2	≈270
Electronegativity	3.98	3.16	2.96	2.66	2.20
Ionic radius (Å)	1.33	1.81	1.96	2.20	≈2.27
Atomic radius (Å)	0.64	0.99	1.14	1.33	1.40
Enthalpy of fusion [†]	0.511	6.410	10.55	15.78	23.9
Enthalpy of vaporization [†]	6.531	20.347	29.56	41.950	
Bond enthalpy of M ₂ [†]	158	243	193	151	110
Standard reduction potential (volts)	2.87 F ₂ /F ⁻	1.358 Cl ₂ /Cl ⁻	1.065 Br ₂ /Br ⁻	0.535 I ₂ /I ⁻	≈0.2 At ₂ /At ⁻

[†] In kilojoules per mole.

The Noble Gases (Group VIII Elements)

	Helium	Neon	Argon	Krypton	Xenon	Radon
Atomic number	2	10	18	36	54	86
Atomic mass	4.00260	20.1797	39.948	83.80	131.29	(222)
Melting point (°C)	-272.2	-248.67	-189.2	-156.6	-111.9	-71
	(26 atm)					
Boiling point (°C)	-268.934	-246.048	-185.7	-152.30	-107.1	-61.8
Density at 25°C (g cm ⁻³)	0.147	1.207	1.40	2.155	3.52	4.4
	(-270.8°C)	(-246.1°C)	(-186°C)	(-152.9°C)	(-109°C)	(-52°C)
Color	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
Ground-state electron configuration	1s ²	[He]2s ² 2p ⁶	[Ne]3s ² 3p ⁶	[Ar]3d ¹⁰ 4s ² 4p ⁶	[Kr]4d ¹⁰ 5s ² 5p ⁶	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶
Ionization energy [†]	2372.3	2080.6	1520.5	1350.7	1170.4	1037.0
Electron affinity [†]	<0	<0	<0	<0	<0	<0
Atomic radius (Å)	0.32	0.69	0.97	1.10	1.30	1.45
Enthalpy of fusion [†]	0.02093	0.3345	1.176	1.637	2.299	2.9
Enthalpy of vaporization [†]	0.1005	1.741	6.288	9.187	12.643	18.4

The Transition Elements

	Scandium	Yttrium	Lutetium	Titanium	Zirconium	Hafnium
Atomic number	21	39	71	22	40	72
Atomic mass	44.95591	88.90585	174.967	47.88	91.224	178.49
Melting point (°C)	1541	1522	1656	1660	1852	2227
Boiling point (°C)	2831	3338	3315	3287	4504	4602
Density at 25°C (g cm ⁻³)	2.989	4.469	9.840	4.54	6.506	13.31
Color	Silver	Silver	Silver	Silver	Gray-white	Silver
Ground-state electron configuration	[Ar]3d ¹ 4s ²	[Kr]4d ¹ 5s ²	[Xe]4f ¹⁴ 5d ¹ 6s ²	[Ar]3d ² 4s ²	[Kr]4d ² 5s ²	[Xe]4f ¹⁴ 5d ² 6s ²
Ionization energy [†]	631	616	523.5	658	660	654
Electron affinity [†]	18.1	29.6	≈50	7.6	41.1	≈0
Electronegativity	1.36	1.22	1.27	1.54	1.33	1.30
Ionic radius (Å)	0.81	0.93	0.848 (+3)	0.68	0.80	0.78
Atomic radius (Å)	1.61	1.78	1.72	1.45	1.59	1.56
Enthalpy of fusion [†]	11.4	11.4	19.2	18.62	20.9	25.5
Enthalpy of vaporization [†]	328	425	247	426	590	571
Standard reduction potential (volts)	-2.08	-2.37	-2.30	-0.86	-1.43	-1.57
	Sc ³⁺ /Sc	Y ³⁺ /Y	Lu ³⁺ /Lu	TiO ₂ ,H ⁺ /Ti	ZrO ₂ ,H ⁺ /Zr	HfO ₂ ,H ⁺ /Hf

[†] In kilojoules per mole.*continued*

The Transition Elements (cont.)

	Vanadium	Niobium	Tantalum	Chromium	Molybdenum	Tungsten
Atomic number	23	41	73	24	42	74
Atomic mass	50.9415	92.90638	180.9479	51.9961	95.94	183.85
Melting point (°C)	1890	2468	2996	1857	2617	3410
Boiling point (°C)	3380	4742	5425	2672	4612	5660
Density at 25°C (g cm ⁻³)	6.11	8.57	16.654	7.18	10.22	19.3
Color	Silver-white	Gray-white	Steel gray	Silver	Silver	Steel gray
Ground-state electron configuration	[Ar]3d ³ 4s ²	[Kr]4d ⁴ 5s ¹	[Xe]4f ¹⁴ 5d ³ 6s ²	[Ar]3d ⁵ 4s ¹	[Kr]4d ⁵ 5s ¹	[Xe]4f ¹⁴ 5d ⁴ 6s ²
Ionization energy [†]	650	664	761	652.8	684.9	770
Electron affinity [†]	50.7	86.2	31.1	64.3	72.0	78.6
Electronegativity	1.63	1.60	1.50	1.66	2.16	2.36
Ionic radius (Å)	0.59 (+5) 0.63 (+4) 0.74 (+3) 0.88 (+2)	0.69 (+5) 0.74 (+4)	0.68 (+5)	0.63 (+3) 0.89 (+2)	0.62 (+6) 0.70 (+4)	0.62 (+6) 0.70 (+4)
Atomic radius (Å)	1.31	1.43	1.43	1.25	1.36	1.37
Enthalpy of fusion [†]	21.1	26.4		20.9	27.8	35.4
Enthalpy of vaporization [†]	512	722	781	394.7	589.2	819.3
Standard reduction potential (volts)	-1.2 V ²⁺ /V	-0.62 Nb ₂ O ₅ ,H ⁺ /Nb	-0.71 Ta ₂ O ₅ ,H ⁺ /Ta	-0.74 Cr ³⁺ /Cr	0.0 H ₂ MoO ₄ ,H ⁺ /Mo	-0.09 WO ₃ ,H ⁺ /W
	Manganese	Technetium	Rhenium	Iron	Ruthenium	Osmium
Atomic number	25	43	75	26	44	76
Atomic mass	54.93805	(98)	186.207	55.847	101.07	190.2
Melting point (°C)	1244	2172	3180	1535	2310	3045
Boiling point (°C)	1962	4877	5627	2750	3900	5027
Density at 25°C (g cm ⁻³)	7.21	11.50	21.02	7.874	12.41	22.57
Color	Gray-white	Silver-gray	Silver	Gray	White	Blue-white
Ground-state electron configuration	[Ar]3d ⁵ 4s ²	[Kr]4d ⁵ 5s ²	[Xe]4f ¹⁴ 5d ⁵ 6s ²	[Ar]3d ⁶ 4s ²	[Kr]4d ⁷ 5s ¹	[Xe]4f ¹⁴ 5d ⁶ 6s ²
Ionization energy [†]	717.4	702	760	759.3	711	840
Electron affinity [†]	< 0	≈53	≈14	15.7	≈100	≈106
Electronegativity	1.55	1.90	1.90	1.90	2.2	2.20
Ionic radius (Å)	0.80 (+2)		0.56 (+7) 0.27 (+4)	0.60 (+3) 0.72 (+2)	0.67 (+4)	0.69 (+6) 0.88 (+4)
Atomic radius (Å)	1.37	1.35	1.34	1.24	1.32	1.34
Enthalpy of fusion [†]	14.6	23.8	33.1	15.19	26.0	31.8
Enthalpy of vaporization [†]	279	585	778	414	649	678
Standard reduction potential (volts)	-0.183 Mn ³⁺ /Mn	0.738 TcO ₄ ⁻ ,H ⁺ /TcO ₂	0.3 Re ³⁺ /Re	-0.036 Fe ³⁺ /Fe	0.49 Ru ⁴⁺ /Ru ³⁺	0.85 OsO ₄ ,H ⁺ /Os

[†] In kilojoules per mole.*continued*

The Transition Elements (cont.)

	Cobalt	Rhodium	Iridium	Nickel	Palladium	Platinum
Atomic number	27	45	77	28	46	78
Atomic mass	58.93320	102.90550	192.22	58.69	106.42	195.08
Melting point (°C)	1459	1966	2410	1453	1552	1772
Boiling point (°C)	2870	3727	4130	2732	3140	3827
Density at 25°C (g cm ⁻³)	8.9	12.41	22.42	8.902	12.02	21.45
Color	Steel gray	Silver	Silver	Silver	Steel white	Silver
Ground-state electron configuration	[Ar]3d ⁷ 4s ²	[Kr]4d ⁸ 5s ¹	[Xe]4f ¹⁴ 5d ⁷ 6s ²	[Ar]3d ⁸ 4s ²	[Kr]4d ¹⁰	[Xe]4f ¹⁴ 5d ⁹ 6s ¹
Ionization energy [†]	758	720	880	736.7	805	868
Electron affinity [†]	63.8	110	151	111.5	51.8	205.1
Electronegativity	1.88	2.28	2.20	1.91	2.20	2.28
Ionic radius (Å)	0.63 (+3) 0.72 (+2)	0.68 (+3)	0.68 (+4)	0.69 (+2)	0.65 (+4) 0.80 (+2)	0.65 (+4) 0.80 (+2)
Atomic radius (Å)	1.25	1.34	1.36	1.25	1.38	1.37
Enthalpy of fusion [†]	16.2	21.5	26.4	17.6	17.6	19.7
Enthalpy of vaporization [†]	373	557	669	428	353	564
Standard reduction potential (volts)	-0.28 Co ²⁺ /Co	1.43 Rh ⁴⁺ /Rh ³⁺	0.1 Ir ₂ O ₃ /Ir, OH ⁻	-0.23 Ni ²⁺ /Ni	0.83 Pd ²⁺ /Pd	1.2 Pt ²⁺ /Pt
	Copper	Silver	Gold	Zinc	Cadmium	Mercury
Atomic number	29	47	79	30	48	80
Atomic mass	63.546	107.8682	196.96654	65.39	112.411	200.59
Melting point (°C)	1083.4	961.93	1064.43	419.58	320.9	-38.87
Boiling point (°C)	2567	2212	2807	907	765	356.58
Density at 25°C (g cm ⁻³)	8.96	10.50	19.32	7.133	8.65	13.546
Color	Red	Silver	Yellow	Blue-white	Blue-white	Silver
Ground-state electron configuration	[Ar]3d ¹⁰ 4s ¹	[Kr]4d ¹⁰ 5s ¹	[Xe]4f ¹⁴ 5d ¹⁰ 6s ¹	[Ar]3d ¹⁰ 4s ²	[Kr]4d ¹⁰ 5s ²	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²
Ionization energy [†]	745.4	731.0	890.1	906.4	867.7	1007.0
Electron affinity [†]	118.5	125.6	222.749	< 0	< 0	< 0
Electronegativity	1.90	1.93	2.54	1.65	1.69	2.00
Ionic radius (Å)	0.72 (+2) 0.96 (+1)	0.89 (+2) 1.26 (+1)	0.85 (+2) 1.37 (+1)	0.74 (+2)	0.97 (+2) 1.14 (+1)	1.10 (+2) 1.27 (+1)
Atomic radius (Å)	1.28	1.44	1.44	1.34	1.49	1.50
Enthalpy of fusion [†]	13.3	11.95	12.36	7.39	6.11	2.300
Enthalpy of vaporization [†]	304	285	365	131	112	59.1
Standard reduction potential (volts)	0.340 Cu ²⁺ /Cu	0.800 Ag ⁺ /Ag	1.42 Au ³⁺ /Au	-0.763 Zn ²⁺ /Zn	-0.403 Cd ²⁺ /Cd	0.796 Hg ₂ ²⁺ /Hg

[†] In kilojoules per mole.

The Lanthanide Elements

	Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium
Atomic number	57	58	59	60	61	62	63
Atomic mass	138.9055	140.115	140.90765	144.24	(145)	150.36	151.965
Melting point (°C)	921	798	931	1010	≈1080	1072	822
Boiling point (°C)	3457	3257	3212	3127	≈2400	1778	1597
Density at 25°C (g cm ⁻³)	6.145	6.657	6.773	6.80	7.22	7.520	5.243
Color	Silver	Gray	Silver	Silver		Silver	Silver
Ground-state electron configuration	[Xe]5d ¹ 6s ²	[Xe]4f ¹ 5d ¹ 6s ²	[Xe]4f ³ 6s ²	[Xe]4f ⁴ 6s ²	[Xe]4f ⁵ 6s ²	[Xe]4f ⁶ 6s ²	[Xe]4f ⁷ 6s ²
Ionization energy [†]	538.1	528	523	530	536	543	547
Electron affinity [†]	50			est. 50			
Electronegativity	1.10	1.12	1.13	1.14		1.17	
Ionic radius (Å)	1.15	0.92 (+4) 1.034 (+3)	0.90 (+4) 1.013 (+3)	0.995 (+3)	0.979 (+3)	0.964 (+3)	0.950 (+3) 1.09 (+2)
Atomic radius (Å)	1.87	1.82	1.82	1.81	1.81	1.80	2.00
Enthalpy of fusion [†]	5.40	5.18	6.18	7.13	12.6	8.91	(10.5)
Enthalpy of vaporization [†]	419	389	329	324		207	172
Standard reduction potential (volts)	-2.37 La ³⁺ /La	-2.335 Ce ³⁺ /Ce	-2.35 Pr ³⁺ /Pr	-2.32 Nd ³⁺ /Nd	-2.29 Pm ³⁺ /Pm	-2.30 Sm ³⁺ /Sm	-1.99 Eu ³⁺ /Eu
	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium
Atomic number	64	65	66	67	68	69	70
Atomic mass	157.25	158.92534	162.50	164.93032	167.26	168.93421	173.04
Melting point (°C)	1311	1360	1409	1470	1522	1545	824
Boiling point (°C)	3233	3041	2335	2720	2510	1727	1193
Density at 25°C (g cm ⁻³)	7.900	8.229	8.550	8.795	9.066	9.321	6.965
Color	Silver	Silver-gray	Silver	Silver	Silver	Silver	Silver
Ground-state electron configuration	[Xe]4f ⁷ 5d ¹ 6s ²	[Xe]4f ⁹ 6s ²	[Xe]4f ¹⁰ 6s ²	[Xe]4f ¹¹ 6s ²	[Xe]4f ¹² 6s ²	[Xe]4f ¹³ 6s ²	[Xe]4f ¹⁴ 6s ²
Ionization energy [†]	592	564	572	581	589	596.7	603.4
Electron affinity [†]				est. 50			
Electronegativity	1.20		1.22	1.23	1.24	1.25	
Ionic radius (Å)	0.938 (+3)	0.84 (+4) 0.923 (+3)	0.908 (+3)	0.894 (+3)	0.881 (+3)	0.869 (+3)	0.858 (+3) 0.93 (+2)
Atomic radius (Å)	1.79	1.76	1.75	1.74	1.73	1.72	1.94
Enthalpy of fusion [†]	15.5	16.3	17.2	17.2	17.2	18.2	9.2
Enthalpy of vaporization [†]	301	293	165	285	280	240	165
Standard reduction potential (volts)	-2.28 Gd ³⁺ /Gd	-2.31 Tb ³⁺ /Tb	-2.29 Dy ³⁺ /Dy	-2.33 Ho ³⁺ /Ho	-2.32 Er ³⁺ /Er	-2.32 Tm ³⁺ /Tm	-2.22 Yb ³⁺ /Yb

[†] In kilojoules per mole.

The Actinide Elements

	Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium
Atomic number	89	90	91	92	93	94	95
Atomic mass	(227)	232.0381	231.03588	238.0289	(237)	(244)	(243)
Melting point (°C)	1050	1750	1600	1132.3	640	624	994
Boiling point (°C)	3200	4790		3818	2732	3232	2607
Density at 25°C (g cm ⁻³)	10.07	11.72	15.37	18.95	20.25	19.84	13.67
Color	Silver	Silver	Silver	Silver	Silver	Silver	Silver
Ground-state electron configuration	[Rn]6d ¹ 7s ²	[Rn]6d ² 7s ²	[Rn]5f ² 6d ¹ 7s ²	[Rn]5f ³ 6d ¹ 7s ²	[Rn]5f ⁴ 6d ¹ 7s ²	[Rn]5f ⁶ 7s ²	[Rn]5f ⁷ 7s ²
Ionization energy [†]	499	587	568	587	597	585	578
Electronegativity	1.1	1.3	1.5	1.38	1.36	1.28	1.3
Ionic radius (Å)	1.11 (+3)	0.99 (+4)	0.89 (+5) 0.96 (+4) 1.05 (+3)	0.80 (+6) 0.93 (+4) 1.03 (+3)	0.71 (+7) 0.92 (+4) 1.01 (+3)	0.90 (+4) 1.00 (+3)	0.89 (+4) 0.99 (+3)
Atomic radius (Å)	1.88	1.80	1.61	1.38	1.30	1.51	1.84
Enthalpy of fusion [†]	14.2	18.8	16.7	12.9	9.46	3.93	14.4
Enthalpy of vaporization [†]	293	575	481	536	337	348	238
Standard reduction potential (volts)	-2.6 Ac ³⁺ /Ac	-1.90 Th ⁴⁺ /Th	-1.0 PaO ₂ ⁺ , H ⁺ /Pa	-1.8 U ³⁺ /U	-1.9 Np ³⁺ /U	-2.03 Pu ³⁺ /Pu	-2.32 Am ³⁺ /Am
	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium
Atomic number	96	97	98	99	100	101	102
Atomic mass	(247)	(247)	(251)	(252)	(257)	(258)	(259)
Melting point (°C)	1340						
Boiling point (°C)							
Density at 25°C (g cm ⁻³)	13.51	14					
Color	Silver	Silver	Silver	Silver			
Ground-state electron configuration	[Rn]5f ⁷ 6d ¹ 7s ²	[Rn]5f ⁹ 7s ²	[Rn]5f ¹⁰ 7s ²	[Rn]5f ¹¹ 7s ²	[Rn]5f ¹² 7s ²	[Rn]5f ¹³ 7s ²	[Rn]5f ¹⁴ 7s ²
Ionization energy [†]	581	601	608	619	627	635	642
Electronegativity	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Ionic radius (Å)	0.88 (+4) 1.01 (+3) 1.19 (+2)	0.87 (+4) 1.00 (+3) 1.18 (+2)	0.86 (+4) 0.99 (+3) 1.17 (+2)	0.85 (+4) 0.98 (+3) 1.16 (+2)	0.84 (+4) 0.97 (+3) 1.15 (+2)	0.84 (+4) 0.96 (+3) 1.14 (+2)	0.83 (+4) 0.95 (+3) 1.13 (+2)
Standard reduction potential (volts)	-2.06 Cm ³⁺ /Cm	-1.05 Bk ³⁺ /Bk	-1.93 Cf ³⁺ /Cf	-2.0 Es ³⁺ /Es	-1.96 Fm ³⁺ /Fm	-1.7 Md ³⁺ /Md	-1.2 No ³⁺ /No

[†] In kilojoules per mole.**The Transactinide Elements[†]**

	Lawrencium	Rutherfordium	Dubnium	Seaborgium	Bohrium	Hassium	Meitnerium
Atomic number	103	104	105	106	107	108	109
Atomic mass	(262)	(261)	(262)	(263)	(262)	(265)	(266)
Melting point (°C)	1600						
Ground-state electron configuration	[Rn]5f ¹⁴ 7s ² 7p ¹	[Rn]5f ¹⁴ 6d ² 7s ²	[Rn]5f ¹⁴ 6d ³ 7s ²	[Rn]5f ¹⁴ 6d ⁴ 7s ²	[Rn]5f ¹⁴ 6d ⁵ 7s ²	[Rn]5f ¹⁴ 6d ⁶ 7s ²	[Rn]5f ¹⁴ 6d ⁷ 7s ²
Ionization energy		490	640	730	660	750	840

[†] All missing data are unknown.

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