

Chapter 1 Basic Principles

Certain basic principles are fundamental to our understanding of how natural systems work. In this chapter we will consider the structure of the atom and other principles that are necessary in order to describe the chemical and biological processes that can occur in the natural environment. Much of this material would be covered in an introductory university chemistry course. Hence, this chapter will serve as a review. In addition, concepts such as *steady state* and *box models*, widely used in describing interactions in the natural environment, but unlikely to have been covered in a basic chemistry course, will also be developed.

THE ATOM

We can envision two possible models of matter, one in which matter is continually divisible into smaller units (a continuous view of matter) and one in which there is a limit to the size of the units (a discontinuous view of matter). Which is correct was largely a philosophical issue until the early 1800s, when Dalton developed a testable model of matter composed of tiny, indestructible particles (atoms). The structure of atoms is fundamental to our understanding of the physical world.

Atoms were initially viewed as solid, impenetrable units, i.e., the smallest recognizable form of matter. With the discovery of the electron in the late 19th century, the plum pudding model was proposed by Thomson. In this model the negatively charged electrons were seen to be embedded in a positively charged matrix—like raisins in a plum pudding. In the early 20th century, Rutherford conducted an experiment in which he fired a beam of alpha particles (helium nuclei) at a sheet of gold foil. Many of the alpha particles passed through the gold foil, as expected, but some bounced back at high angles. Rutherford interpreted these results as follows. Most of the atom must consist of empty space; the alpha particles passed through unimpeded. But somewhere in the atom there must be a concentration of mass that is responsible for the deflection of the alpha particles. Because the deflections were relatively rare, he concluded that the mass must be concentrated in a small volume, which he referred to as the nucleus. In this model the nucleus is seen to be positively charged, and it is circled by negatively charged electrons. However, in terms of classical physics the Rutherford atom is unstable because the electrons should quickly spiral into the nucleus; i.e., an atom would have a very short lifetime—clearly a problem because matter had been around for billions of years. This problem was solved

by Bohr (the Bohr atom), who proposed that the electrons could only exist in stable orbits at certain discrete distances from the nucleus.

The Bohr Atom

The mathematical description of the Bohr atom is straightforward, and an understanding of the Bohr atom provides an insight into the origin of atomic spectra. We start with a single electron (charge = -1) revolving around a nucleus consisting of one proton (charge = $+1$). For a stable atom, the electrostatic attraction between the electron and the proton must equal the centrifugal force. Thus,

$$k \frac{e^2}{r^2} = \frac{mv^2}{r} \quad (1-1)$$

Electrostatic force = Centrifugal force

where k is a proportionality constant that depends on the units used for the electrostatic charge and the distance between the charges, e is the charge of the electron, r is the distance between the proton and the electron, m is the mass of the electron, and v is the velocity of the electron in its orbit. Bohr proposed that the electron could exist only at certain discrete distances from the nucleus; i.e., the position of the electron was quantized. The allowable distances were determined by restricting the angular momentum of the electron to multiples of $h/2\pi$, where h is Planck's constant ($h = 6.62607 \times 10^{-34}$ J s). This relationship can be written

$$mvr = \frac{nh}{2\pi} \quad (1-2)$$

where $n = 1, 2, 3$, etc. and n is the first, or principal, quantum number. From equation 1-1,

$$mvr = k \frac{e^2}{v} \quad (1-3)$$

Combining equations 1-2 and 1-3 gives

$$k \frac{e^2}{v} = \frac{nh}{2\pi} \quad (1-4)$$

For any particular allowed orbital radius, the velocity of the electron can be determined by solving equation 1-2 for velocity.

$$v = \frac{nh}{2\pi mr} \quad (1-5)$$

Substituting equation 1–5 into equation 1–4 and solving for r gives

$$r = \frac{n^2 h^2}{4\pi^2 m k e^2} \quad (1-6)$$

The energy of the atom is the sum of the kinetic and potential energies. The kinetic energy is due to the revolution of the electron around the nucleus, and the potential energy is due to the electrostatic attraction between the positively charged nucleus and the negatively charged electron.

$$E = \underbrace{\frac{1}{2} m v^2}_{\text{kinetic energy}} - \underbrace{k \frac{e^2}{r}}_{\text{potential energy}} \quad (1-7)$$

Substituting for r (from equation 1–6) gives

$$E = -\frac{2\pi^2 m k^2 e^4}{n^2 h^2} \quad (1-8)$$

For the Bohr atom, the energy of each allowed orbital is determined solely by the principal quantum number. In atoms more complicated than the Bohr atom—i.e., atoms of atomic number greater than 1—the picture becomes more complex, as will be described in the next section.

Before we leave the Bohr atom, let us consider what will happen if an electron moves from one orbit to another. If the radius of the electron orbit was zero, the electron would be at the nucleus, the principal quantum number would be zero, and the atom would have an infinite negative energy. As the electron moves away from the nucleus, the energy becomes less negative. Hence, if an electron moves from a lower to a higher orbit, it must gain energy, and if it moves from a higher to a lower orbit, it must lose energy. When an electron moves from a higher to a lower orbit, the energy is released as a particular wavelength of electromagnetic radiation (EM radiation). Einstein's famous photoelectric experiment (for which he was awarded the Nobel prize) demonstrated that in certain situations EM radiation behaved as a particle (called a *photon*). The relationship between the energy of the photon and the frequency of emitted EM radiation is

$$E = h\nu \quad (1-9)$$

where h is Planck's constant and ν is the frequency of the EM radiation. The velocity of electromagnetic waves is related to frequency (ν) and wavelength (λ) as follows:

$$v = \nu\lambda \quad (1-10)$$

Combining equations 1-9 and 1-10 to find the relationship between energy and wavelength gives

$$E = \frac{hc}{\lambda} \quad (1-11)$$

where c is the velocity of electromagnetic waves in a vacuum ($c = 3.0 \times 10^8 \text{ m s}^{-1}$).

EXAMPLE 1-1 Calculate the energy released when an electron moves from the third allowed orbit to the second allowed orbit. The mass of the electron (m) = $9.109 \times 10^{-31} \text{ kg}$, the charge of the electron (e) = $1.602 \times 10^{-19} \text{ C}$, and $k = 8.98742 \times 10^9 \text{ N m}^2 \text{ C}^{-2}$. For $n = 2$,

$$\begin{aligned} E &= \frac{(2)(\pi)^2 (9.109 \times 10^{-31} \text{ kg})(8.98742 \times 10^9 \text{ N m}^2 \text{ C}^{-2})^2 (1.602 \times 10^{-19} \text{ C})^4}{(2)^2 (6.62607 \times 10^{-34} \text{ J s})^2} \\ &= -5.4403 \times 10^{-19} \text{ J} \end{aligned}$$

For $n = 3$, $E = -2.4179 \times 10^{-19} \text{ J}$. The energy released when the electron moves from orbit 3 to orbit 2 is

$$\Delta E = E_3 - E_2 = -2.4179 \times 10^{-19} \text{ J} - (-5.4403 \times 10^{-19} \text{ J}) = 3.0224 \times 10^{-19} \text{ J}$$

The wavelength of the emitted radiation is

$$\lambda = \frac{hc}{E} = \frac{(6.62607 \times 10^{-34} \text{ J s})(3.0 \times 10^8 \text{ m s}^{-1})}{3.0224 \times 10^{-19} \text{ J}} = 6.578 \times 10^{-7} \text{ m} = 658 \text{ nm}$$

It is known that under the proper conditions of excitation atomic hydrogen will emit EM radiation of particular wavelengths. These so-called lines (as seen in a spectrograph) can be grouped into series, which are named after the person who discovered the particular series. One of these series, called the Balmer series, has a line at $\lambda = 656.3 \text{ nm}$, very close to the wavelength just calculated. The interpretation is that this spectral line is due to the movement of an electron from the third to the second orbit in hydrogen. The set of observed spectral lines is characteristic

of atomic hydrogen.

Beyond the Bohr Atom—Quantum Mechanics

Although the Bohr model was successful in predicting spectral observations for hydrogen atoms, it failed to adequately describe the spectral emission of atoms of higher atomic number. The **atomic number** of an atom is *the number of protons (positively charged particles) in the nucleus*. The number of protons in the nucleus determines the element (i.e., 1 proton, hydrogen; 2—helium; 3—lithium; etc.). This problem was addressed by Heisenberg and Schrödinger. It was concluded that the fundamental problem with the Bohr model was that it considered electrons to be particles whose position in space could be determined with certainty. Work by de Broglie had shown that particles can have wave properties. The relationship between the wavelength (λ) of particles, their mass (m), and velocity (v) is expressed by the de Broglie equation

$$\lambda = \frac{h}{mv} \quad (1-12)$$

EXAMPLE 1–2 Calculate the de Broglie wavelength for an electron in the first orbit ($n = 1$) of the Bohr atom.

From equation 1–6, $r = 5.29 \times 10^{-11}$ m. Substituting into equation 1–5 gives $v = 2.189 \times 10^6$ m s⁻¹. The de Broglie wavelength for the electron is

$$\lambda = \frac{h}{mv} = \frac{6.62607 \times 10^{-34} \text{ J s}}{(9.109 \times 10^{-31} \text{ kg})(2.189 \times 10^6 \text{ m s}^{-1})} = 3.32 \times 10^{-10} \text{ m}$$

This wavelength is similar to that of energetic X rays.

Schrödinger used the wave properties of the electron to develop the now well-known, if not necessarily well-understood, Schrödinger wave model of the atom. In this model the most probable position of the electron is at a node developed in a standing wave. Multiple nodes are possible, each representing a principal quantum number. In three dimensions, nodes may form along three principal axes, giving rise to three quantum numbers. A fourth quantum number deals with the spin of the electron. These quantum numbers are summarized in Table 1–1. The magnetic quantum number arises when the atom is subjected to a magnetic field. The spin

quantum number indicates the direction of spin of an electron in a particular orbital. An orbital cannot contain more than two electrons, and the two electrons must spin in opposite directions (the *Pauli exclusion principle*, which states that *no two electrons in an atom can have the same quantum numbers*). Four types of wave functions are possible, designated *s*, *p*, *d*, and *f*, which describe the orientation of the electron orbitals in space (Figure 1-1). Only the *s*, *p*, and *d* orbitals are shown in Figure 1–1. The *f* orbitals cannot be pictured in two dimensions. The relationship between the quantum numbers and the electron orbitals is given in Table 1–2.

Table 1-1 Summary of Quantum Numbers

Name	Symbol	Values
Principal	n	1, 2, 3, . . . , ∞
Azimuthal	l	$n - 1, n - 2, n - 3, \dots, 0$
Magnetic	m	$0, \pm 1, \pm 2, \dots, \pm(l - 1), \pm 1$
Spin	s	$\pm \frac{1}{2}$

Table 1-2 Relationship between Quantum Numbers and Electron Orbitals

n	L	M	Number of	Number of	Designation
1	0	0	1	1	1s
2	0	0	2	1	2s
	1	-1, 0, 1		3	2p
3	0	0	3	1	3s
	1	-1, 0, 1		3	3p
	2	-2, -1, 0, 1, 2		5	3d
4	0	0	4	1	4s
	1	-1, 0, -1		3	4p
	2	-2, -1, 0, 1, 2		5	4d
	3	-3, -2, -1, 0, 1, 2, 3		7	4f

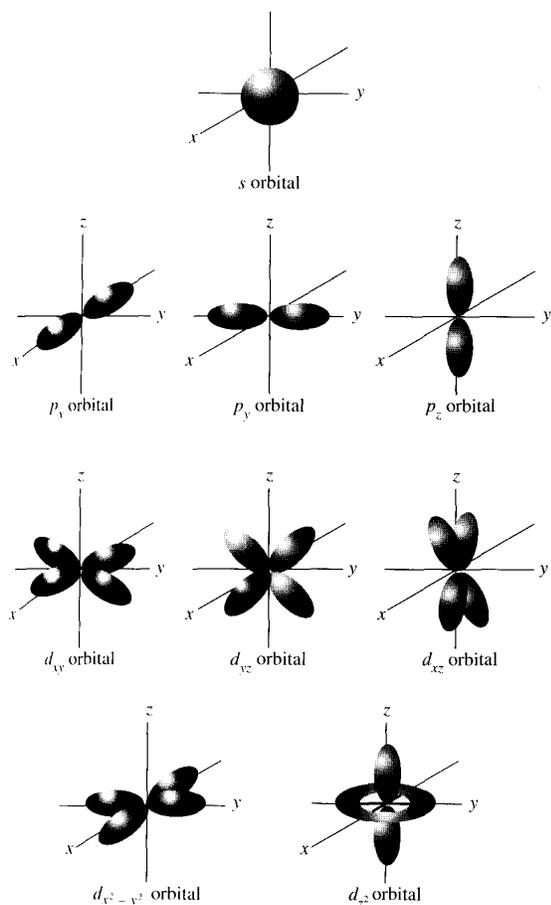


Figure 1-1 Shape of various electron orbitals. From Brownlow (1996).

It is important to note that these orbital shapes actually represent probability distributions for the location of the electron. The *Heisenberg uncertainty principle* tells us that *it is impossible to simultaneously measure both the position and velocity of a particle*. The very act of measurement will disturb the particle. Hence, the position of a particle, in this case an electron, is only approximately known. Thus, the orbitals shown in Figure 1–1 represent the most probable location of an electron at any particular time. All distances are possible, but some are less probable. What this means is that there are two endpoints for the position of the electron—the nucleus and infinity—both of which have zero probability. At any instant the electron can occupy a position between these two end members, but its most likely position is at a distance defined by the allowable electron orbitals.

By applying the principles of quantum mechanics we can now build the various elements of

the periodic table. We do this by adding electrons and protons in equal numbers to the basic hydrogen atom. Remember that the element is determined by the nucleus, i.e., the number of protons in the nucleus. The addition of electrons conforms to the following rules:

1. An electron will enter the available orbital with the lowest energy. The overall energy of the atom is minimized.
2. For each set of orbitals (s , p , d , f) the electrons will first be added singly to each available orbital. After all the orbitals in a set have a single electron, subsequent electrons can enter these orbitals if they have the opposite spin.
3. Atoms attain their maximum stability when the available orbitals are either completely filled, half-filled, or empty.

Because of the electrostatic attractions between the positively charged nucleus and the negatively charged electrons, the filling of the orbitals does not proceed in simple numerical order. For example, the $4s$ orbital is at a lower energy than the $3d$ orbital. Hence, electrons are first added to the $4s$ orbital and subsequent electrons are then added to the $3d$ orbital. This sequence of additions is responsible for the transition series metals in the periodic table. The relative energies of the various orbitals, as a function of atomic number, are shown in Figure 1–2.

The sequence in which the subshells are filled is given in Appendix I. In the periodic table the elements are grouped according to their electronic structure. Row 1 represents the filling of the $1s$ orbital, row 2 the filling of the $2s$ and $2p$ orbitals, and row 3 the filling of the $3s$ and $3p$ orbitals. Row 4 starts with the filling of the $4s$ orbitals followed by the filling of the $3d$ orbitals. This occurs because the $4s$ orbital is at a lower energy than the $3d$ orbitals. The filling of the $3d$ orbitals forms a sequence of 10 elements that behave similarly because all but Cr and Cu have two $4s$ electrons in their outer shell. A similar situation exists for row 5, in which the $5s$ orbital is filled followed by filling of the $4d$ orbitals, leading to another sequence of 10 elements that show similar chemical behaviors. Note that the $4f$ orbitals do not yet contain any electrons. The filling of the $4f$ orbitals occurs in row 6, giving rise to the 14 elements of the lanthanide series. A similar situation exists with respect to the filling of the $5f$ orbitals, which occurs in row 7, giving rise to the 14 elements of the actinide series.

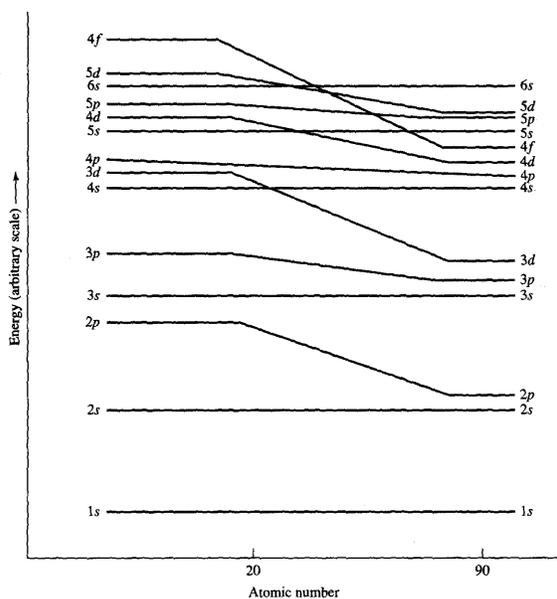


Figure 1–2 Variation of the energy levels for the various subshells as a function of atomic number. From Brownlow (1996).

Ionization and Valences

It was noted earlier that atoms are most stable when their orbitals are filled, half-filled, or empty. This observation allows us to understand why different elements show particular valences. **Valence** is the combining capacity of atoms. This capacity can be interpreted in several ways, i.e., the number of hydrogen atoms that can combine with a particular atom or the number of single bonds it can form with other atoms. Some authors consider valence to be a pure number, whereas others assign charges to valence. We will use the latter convention. *Atoms that have gained or lost electrons* are called **ions**. If the *atom has gained electrons and has a net negative charge*, it is an **anion**; and if an *atom has lost electrons and has a net positive charge*, it is a **cation**. The *energy required to remove an electron from an atom and place it at an infinite distance* is the **ionization potential**. In any given row of the periodic table, as we move from left to right the ionization potential tends to increase; i.e., it becomes more difficult to remove electrons from the atom. Hence, elements on the left-hand side of the periodic table tend to form cations, and those on the right-hand side tend to form anions.

Consider the element sodium (Na). The 1s, 2s, and 2p orbitals are completely filled. The

outer $3s$ orbital contains 1 electron. The most stable configuration for this atom is one in which all the shells ($n = 1$ and $n = 2$) are filled. Because there is only a single $3s$ electron, it is readily lost, leading to a cation with a $+1$ charge. On the other hand, chlorine (Cl) has 5 electrons in the $3p$ orbital. A complete subshell can be formed by adding an electron to the $3p$ orbital, leading to an anion with a charge of -1 . Argon (Ar) has a completely filled $3p$ orbital; hence, this element neither gains nor loses electrons. The elements in the eighth column of the periodic table are referred to as *noble gases*, because they do not readily combine with other elements. An inspection of the common valences listed in Appendix I will show that most of them can be explained in terms of completely filled, half-filled, or empty orbitals.

Spectra and Elemental Analysis

In Example 1-1 we calculated the energy that would be emitted, and the corresponding wavelength of EM radiation, during a particular electronic transition in the Bohr atom. In the example the electron moved from a higher to a lower orbit, releasing energy. The result is an emission line. If we consider other possible transitions in the Bohr atom from higher orbits to the same orbit, we get a series of emission lines that form, in the case of Example 1-1, the Balmer series. This series of emission lines is characteristic of the neutral hydrogen atom. For other neutral atoms in the periodic table, transitions between orbitals release different amounts of energy, and the resulting emission spectra are different and characteristic for each element. If the atoms have been ionized—i.e., they have gained or lost electrons resulting in a net negative or net positive charge, respectively—the sequence of emission lines will be slightly shifted because the electrostatic attraction between the nucleus and the electrons will have changed. Thus, emission lines are not only characteristic of particular elements but they can also be used to infer the ionization state of an atom. The *spectrum produced when electrons move from higher orbitals to lower orbitals* is called an ***emission spectrum*** (Figure 1-3).

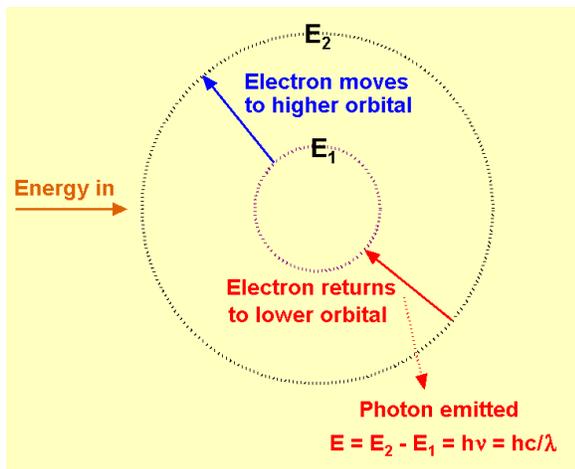


Figure 1–3 An emission spectrum occurs when energy applied to the atom causes an electron to move from a lower orbital to a higher orbital. The electron returns to a lower orbital and emits energy corresponding to the energy difference between the two orbitals ($E_2 - E_1$). Planck’s constant is h , ν is frequency, and λ is wavelength.

Let us suppose that we have a transparent container filled with hydrogen gas. We pass a beam of white light through this container and use a spectroscope to view the beam when it emerges from the other side of the container. We would observe a continuous spectrum (all colors are present) except for certain specific wavelengths for which no light is visible. If we compared the dark bands in the spectrum with the position of the emission lines for neutral hydrogen, we would discover that they are at the same wavelength. We can explain this result as follows (Figure 1–4). The incident beam of white light consists of photons of all possible energies (in the visible region). Those photons that have exactly the same energy as the energy required to move an electron from one orbital to another in the hydrogen atom will interact with the hydrogen atom and move electrons to higher orbitals. The electrons then return to lower orbitals, emitting energy, but the direction of the emitted photons varies randomly through a 360° solid angle. The probability of an emitted photon traveling in exactly the same direction as the beam of white light and entering the spectroscope is improbably small. Thus, what we observe are *missing wavelengths in the spectrum*, referred to as an **absorption spectrum**, and the photons that correspond to these energies (wavelengths) have been absorbed by the hydrogen atoms.

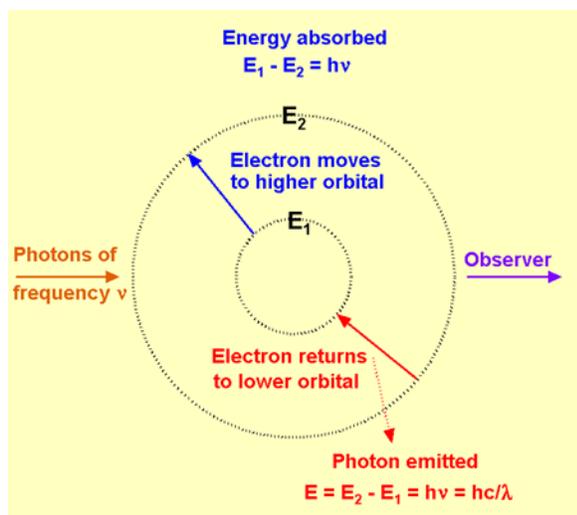


Figure 1–4 An absorption spectrum occurs when photons that have exactly the right energy to move an electron from one orbital to another interact with the atom. When the electron returns to the lower orbital, the emitted photon can travel in any direction. Thus, the observer notices a decrease in the number of photons of this energy (wavelength). Planck’s constant is h , ν is frequency, and λ is wavelength.

Absorption and emission spectra are the basis of a variety of analytical techniques used to determine the elemental composition of natural materials. Examples of analytical techniques that use emission spectra are the electron microprobe (a beam of electrons provides the energy to move the electrons), X-ray fluorescence (X rays provide the energy), ICP-AES (a plasma arc provides the energy), and flame atomic emission spectroscopy (an air-acetylene flame provides the energy). A variety of detectors are used, depending on the energy of the emitted radiation, to measure the rate of photon emission. Absorption spectra are used in atomic absorption spectroscopy (AAS). In this method a hollow cathode tube, the cathode of which consists of a single element or several elements, provides the photon beam. The sample is introduced into a flame or vapor that occupies a position between the source of the photons and the sensor. Changes in the intensity of the beam can be related to the concentration of the element in the flame (or vapor). For example, if the cathode is made of iron, iron atoms in the flame will absorb some of the photons and there will be a decrease in intensity. By relating intensity changes to known concentrations of iron in standards, it is possible to determine the concentration of iron in an unknown. A number of books have been written on these various analytical techniques. The

interested student should consult the literature to learn more about spectroscopic analysis.

The Nucleus

The nucleus of an atom consists of two particles, a proton with a charge of +1 (the same magnitude but opposite sign from the charge on the electron) and a neutron, which has no charge but is essentially equivalent to the proton in terms of mass. The *number of protons in the nucleus* determines the **atomic number**, which identifies the element. For example, an atom with 1 proton is hydrogen, an atom with 10 protons is neon. The nucleus can also contain variable numbers of neutrons. *Atoms that have the same number of protons but different numbers of neutrons* are referred to as **isotopes**. For example, there are three isotopes of hydrogen: common hydrogen, which contains one proton and no neutrons; deuterium, which contains one proton and one neutron; and tritium (a radioactive form of hydrogen), which contains one proton and two neutrons. The *sum of the protons plus neutrons* is the **mass number** of the nucleus. By convention, elemental symbols are written with the atomic number at the lower left of the symbol and the mass number at the upper left (Figure 1-5). The atomic number is often omitted when writing isotopic compositions because it is fixed for a particular element. The upper right is reserved for the valence of the atom. Note that the nucleus consists only of positive charges, and, given the small size of the nucleus, strong repulsive forces are developed. The nucleus is held together by what is referred to as the **strong force**, which acts over a very short range, nominally equal to the diameter of the nucleus. When the size and/or charge of the nucleus becomes too great, the nucleus will break down; i.e., the process known as radioactive decay occurs (see Chapter 6).



Figure 1–5 Standard format for reporting atomic number and mass number. This isotope of beryllium has four protons and five neutrons.

CHEMICAL BONDING

Two or more atoms may combine to form a compound. The compound is held together by chemical bonds. There are four basic types of bonds: ionic, covalent, metallic, and hydrogen (or van der Waals). ***Ionic bonding*** occurs when *cations and anions combine by electrostatic attraction*. The strength of the bond is a function of the distance between the ions and the total charge. ***Covalent bonding*** occurs when *two or more atoms combine by sharing valence electrons*. In practice, most bonds are not purely ionic or purely covalent, but rather are mixed bonds having characteristics of both types. This topic is more fully discussed in Chapter 7. ***Metallic bonding*** occurs in the case of *pure metals in which electrons are freely shared among all the atoms*. Compounds that are held together by metallic bonding are good conductors of electricity. ***Hydrogen bonding***, of which there are many types, involves *polar molecules (such as water) that have a slight charge bias and form weak electrostatic bonds with other ions*. ***Polar covalent bonds***, which are responsible for the polar characteristics of a molecule, arise *when electrons are unequally shared between atoms*. For example, hydrogen fluoride (HF) forms a polar molecule. The F end of the molecule has a slight net negative charge and the H end of the molecule has a slight net positive charge. The interpretation is that the F atom has a stronger attraction for the shared electron than the hydrogen atom. The important case of the polar water molecule will be described in a later section.

ATOMIC AND MOLECULAR WEIGHTS

The modern atomic mass scale is based on ^{12}C . In this system, ^{12}C is given the mass of exactly 12 atomic mass units (amu). In SI units, $1 \text{ amu} = 1.66054 \times 10^{-27} \text{ kg}$. All other isotopes are referenced to ^{12}C . This is done using mass spectrometry, a very precise way of measuring mass ratios. For example, mass spectrometric measurements yield a $^{13}\text{C}/^{12}\text{C}$ ratio = 1.0836129. The mass of ^{13}C is found as follows:

$$\text{Mass } ^{13}\text{C} = \text{Mass } ^{12}\text{C} \times 1.0836129 = 12 \text{ amu} \times 1.0836129 = 13.0033548 \text{ amu}$$

Masses of other isotopes are found in a similar way. The results of these measurements are tabulated in standard references such as the *CRC Handbook of Chemistry and Physics* or *Chart of the Nuclides*.

In nature, most elements occur in more than one isotopic form. For example, there are four

naturally occurring isotopes of iron. The **atomic weight of an element** is the sum of the masses of the individual isotopes weighted according to their abundance. Using iron as an example, the relative abundances and masses (taken from the *CRC Handbook of Chemistry and Physics*) of the iron isotopes and the calculation of the atomic weight of iron is shown here. The abundance of each iron isotope is multiplied by the mass of each isotope. Note that in doing this multiplication percents are converted to decimals, e.g., 5.81% = 0.0581. The proportionate masses of the individual isotopes are then added to give the atomic weight of iron.

Isotope	% Abundance		Mass isotope (amu)	Mass (amu)
⁵⁴ Fe	5.81	×	53.9396	3.1339
⁵⁶ Fe	91.72	×	55.9349	51.3035
⁵⁷ Fe	2.19	×	56.9354	1.2469
⁵⁸ Fe	0.28	×	57.9333	0.1622
at. wt Fe				55.8465

The **mole** (mol) is defined as the number of carbon atoms in exactly 12 grams of pure ¹²C. The **gram-atomic weight** of an element is defined as the atomic weight of the element in grams. In the case of ¹²C, the gram-atomic weight is 12 g. Because the atomic weight of all other isotopes are compared to ¹²C, this means that one gram-atomic weight of any isotope or element contains the same number of atoms. Careful measurements by mass spectrometry have determined the number of atoms in a mole to be 6.022×10^{23} (**Avogadro's number**). From the definition of the mole we can also determine the relationship between amu and grams; i.e., 6.022×10^{23} amu = 1 g and 1 amu = 1.66054×10^{-24} g.

The **gram-molecular weight** is the weight of a compound in grams. For example, halite has the formula NaCl. The atomic weight of Na = 22.9898 and the atomic weight of Cl = 35.4527. The gram-molecular weight of NaCl is 58.4425 g. This corresponds to 1 mole of NaCl, which contains 6.022×10^{23} NaCl molecules.

EXAMPLE 1-3 0.02 g of calcium carbonate (CaCO_3) is dissolved in 1 liter of water. Calculate the moles of calcium carbonate that have dissolved in the water, the moles of Ca^{2+} ions in solution, and the number of Ca^{2+} ions in solution.

The gram-molecular weight of CaCO_3 is calculated as follows:

$$\begin{aligned} 1 \text{ Ca} &= 40.078 \\ 1 \text{ C} &= 12.011 \\ 3 \text{ O} &= \underline{47.997} \\ &100.086 \text{ g} \end{aligned}$$

Moles of $\text{CaCO}_3 = 0.02 \text{ g}/100.086 \text{ g mol}^{-1} = 1.998 \times 10^{-4} \text{ mol}$. There is 1 mole of Ca in each mole of CaCO_3 , so $\text{Ca}^{2+} = 1.998 \times 10^{-4} \text{ mol}$. Number of Ca^{2+} ions in solution = $1.998 \times 10^{-4} \text{ mol} \times 6.022 \times 10^{23} \text{ ions per mol} = 1.203 \times 10^{20} \text{ ions}$.

EXAMPLE 1-4 A 1-liter solution contains $2 \times 10^{-3} \text{ mol}$ of BaSO_4 . Calculate the mass of BaSO_4 dissolved in the water. The gram-molecular weight of $\text{BaSO}_4 = (137.33) + (32.066) + (4)(15.999) = 233.392 \text{ g}$. The grams of BaSO_4 in solution = $2 \times 10^{-3} \text{ mol} \times 233.392 \text{ g mol}^{-1} = 0.467 \text{ g}$.

The ***gram-equivalent weight of an ion*** is the molecular or atomic weight divided by the valence. In the case of an acid or base, it is the number of H^+ or OH^- ions that can be produced when the acid or base is dissolved in water. For example, in BaSO_4 , barium has a valence of 2 and there are two gram-equivalent weights of Ba^{2+} in each mole of BaSO_4 . HCl (hydrochloric acid) and H_2SO_4 (sulfuric acid) are both strong acids that will completely dissociate in water. One mole of HCl will release 1 mole of H^+ ions to solution, so there is one gram-equivalent weight of H^+ in this acid. One mole of H_2SO_4 will release 2 moles of H^+ ions to solution; thus, there are two gram-equivalent weights of H^+ in sulfuric acid.

MEASUREMENT OF CONCENTRATION

Concentrations of elements or compounds in the natural environment have been presented in a variety of ways. In principle, the *Système international d'unités* (SI) should be used, but authors routinely violate this system (although some journals now insist that it be used), and in the older

scientific literature SI units were often not used. In this section the relationships between the most commonly used units are given.

Table 1-3 Units of Absolute Mass Relative to the Kilogram

Unit	Abbreviation	Kilogram
Kilogram	kg	1
Gram	g	1×10^{-3}
Milligram	mg	1×10^{-6}
Microgram	μg	1×10^{-9}
Nanogram	ng	1×10^{-12}

Concentrations can be reported in terms of absolute mass (Table 1-3), and the SI unit is the kilogram (kg). Concentrations can also be reported on a weight per weight basis, giving rise to units such as parts per thousand (ppt or ‰; note that ppt is also used for parts per trillion), parts per million (ppm), or parts per billion (ppb). For example, 1 g of As in 1 kg of soil is equivalent to 1 ppt, and 1 mg of As in 1 kg of soil is equivalent to 1 ppm. When analyzing solutions, concentrations are often reported on a weight per volume basis, for example, 1 mg of As in 1 L (liter) of solution. At room temperature, the density of pure water is close to 1000 kg m^{-3} . A liter is equivalent to $1 \times 10^{-3} \text{ m}^3$. Hence, the mass of 1 L of pure water at room temperature is approximately 1 kg. For very dilute solutions, the amount of dissolved material is relatively small and the mass of the total solution is close to 1 kg per L. On a weight per weight basis, 1 mg of As dissolved in 1 L of water would give a concentration of 1 ppm As. The concentration of elements in freshwater are sometimes given in ppm, but note that, strictly speaking, this is not correct because only on rare occasions will the mass of 1 L of solution be exactly 1 kg.

Concentrations in solutions are reported in a variety of ways, including molarity, molality, normality, and mole fraction. **Molarity** is the *number of moles of solute (the substance that is dissolved) per volume of solution in liters*. **Molality** is the *number of moles of solute per kg of solvent (the material in which the solute is dissolved)*. **Normality** is the *number of equivalents*

per liter of solution. Gram-equivalents were defined in the preceding section. Table 1–4 shows the relationship between molarity and normality for some common acids and bases. **Mole fraction** is the *ratio of the number of moles of a given component to the total number of moles of solution*. Solutions do not have to be liquids. In fact, many minerals (such as the feldspars and carbonates) form solid solution series.

Table 1-4 Molarity and Normality for Several Acids and Bases

Acid or base	Molecular weight	Gram-equivalent weight	Relationship between molarity and normality
HCl	36.5	36.5	1M = 1N
H ₂ SO ₄	98.0	49.0	1M = 2N
H ₃ PO ₄	98.0	32.6	1M = 3N
NaOH	40.0	40.0	1M = 1N
Ca(OH) ₂	74.0	37.0	1M = 2N

EXAMPLE 1–5 An important mineral in many rocks is plagioclase feldspar. The plagioclase feldspars form a solid solution series with the end members pure albite (NaAlSi₃O₈) and pure anorthite (CaAl₂Si₂O₈). A particular plagioclase contains 5 wt% Ca. Calculate the mole fraction of anorthite in the plagioclase. The molecular weights of Ca, Al, Si, and O are, respectively, 40, 27, 28, and 16.

First we calculate the weight percent of anorthite. This is done by multiplying the molecular weight of anorthite by 5, the weight percent of Ca in the plagioclase, and dividing by the atomic weight of Ca. We divide by the atomic weight of Ca because we want to know the ratio of anorthite molecule to Ca.

$$\text{wt\% CaAl}_2\text{Si}_2\text{O}_8 (\text{An}) = \frac{(5)(40 + 2 \times 27 + 2 \times 28 + 8 \times 16)}{40} = 34.8$$

We then subtract the weight percent of anorthite from 100% to give the weight percent of albite.

$$\text{wt\% NaAlSi}_3\text{O}_8 (\text{Ab}) = 100 - 34.8 = 65.2$$

We then determine the relative number of moles of anorthite by dividing the weight percent of anorthite by the molecular weight of the anorthite molecule.

$$\text{Relative number of moles An} = \frac{34.8}{278} = 0.13$$

Similarly, we determine the relative number of moles of albite:

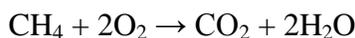
$$\text{Relative number of moles Ab} = \frac{65.2}{262} = 0.25$$

Finally, we determine the mole fraction of anorthite by dividing the relative number of moles of anorthite by the total relative moles of anorthite + albite.

$$\text{Mole fraction An} = \frac{\text{Moles An}}{\text{Moles An} + \text{Ab}} = \frac{0.13}{0.13 + 0.25} = 0.34$$

TYPES OF CHEMICAL REACTIONS

Most chemical reactions are one of the following types: precipitation, acid-base, or oxidation-reduction. During a chemical reaction there is a reorganization of the atoms in one or more substances. Chemical reactions are represented by chemical equations. By convention, the reactants appear on the left-hand side of the equation and the products on the right-hand side of the equation. Consider what happens when methane (natural gas) is combined with oxygen. This reaction can be represented by the following chemical equation:



The reactants are methane (CH₄) and oxygen (O₂), and the products are carbon dioxide (CO₂) and water vapor (H₂O). This is the familiar process of combustion, and heat energy is released. Note that there has been a rearrangement of the atoms in the substances. The carbon in the methane has combined with oxygen to form carbon dioxide, and the hydrogen in the methane has combined with oxygen to form water vapor. The various substances in a chemical reaction are referred to as *species*, *chemical entities that can be*, *ions*, *molecules*, *solid phases*, *gases*, *etc.*

Precipitation reactions occur when two solutions are mixed and a solid, called a ***precipitate***, forms. For example, if a silver nitrate solution is added to a sodium chloride solution, a white precipitate is formed. The chemical reaction can be written

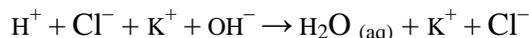


The silver ions in solution have combined with the chloride ions in solution to form an insoluble silver chloride. As written, this is a **complete ionic equation** because it shows all the individual ions. Inspection of the equation reveals that only Ag^+ and Cl^- participate in the reaction to form AgCl . The other ions do not participate in the reaction and are called **spectator ions**. The reaction is more appropriately written as a **net ionic equation**.



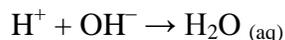
This reaction is the basis of the titration method used to determine the salinity of seawater (see Chapter 10).

Acid–base reactions involve the transfer of protons. By definition, **acids** are *proton donors* and **bases** are *proton acceptors*. We distinguish between two types of acids and bases, strong and weak. Strong acids or bases dissociate completely in water. For example, HCl is a strong acid and when dissolved in water dissociates into H^+ (or H_3O^+) and Cl^- ions. Acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) is a weak acid and only partly dissociates into H^+ and $\text{C}_2\text{H}_3\text{O}_2^-$ ions when dissolved in water. As an example of an acid-base reaction, consider what happens when solutions of hydrochloric acid (HCl) and potassium hydroxide (KOH), a strong acid and strong base, respectively, are mixed. The complete ionic equation can be written



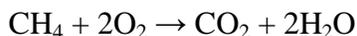
A note about the representation of species in chemical equations: In general, if the species is written as an ion, it is in solution; and if it is written as a neutral compound, it is not in solution. If an uncharged species is in solution, the chemical formula is followed by the subscript (aq). Some textbooks indicate the state of all species by using the subscripts (aq)—aqueous, (s)—solid, (l)—liquid, or (g)—gas.

Note that only the hydrogen and hydroxyl ions are involved in the reaction; the potassium and chlorine ions are spectators. Hence, the net ionic equation is written



Acid-base reactions will be considered in detail in Chapter 3.

Oxidation-reduction reactions occur when there is a transfer of electrons. As an example of an oxidation-reduction reaction we will consider the oxidation of methane as represented by the following equation:



Because the molecules are electrically neutral, the oxidation states of the various atoms in each molecule must sum to zero. Thus, in methane $\text{C} = -4$ and $\text{H} = +1$, in the oxygen molecule the atoms are electrically neutral, in carbon dioxide $\text{C} = +4$ and $\text{O} = -2$, and in water $\text{H} = +1$ and $\text{O} = -2$. During the course of the reaction, the oxidation state of carbon changes from -4 to $+4$ (8 electrons are transferred) and the oxidation state of oxygen changes from 0 to -2 . There is 1 carbon atom on the left-hand side of the equation and 4 oxygen atoms; hence, charge balance is maintained—i.e., 8 electrons from carbon = 2 electrons per oxygen \times 4 oxygen atoms. Note that the oxidation state of hydrogen remains unchanged and it does not participate in the oxidation-reduction reaction. Oxidation-reduction reactions will be considered in detail in Chapter 4.

DETERMINING AND BALANCING A CHEMICAL EQUATION

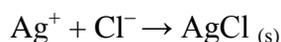
In the previous section we considered different types of chemical reactions. How do we determine which chemical reactions occur and the equations that represent the reactions? While we can use our basic understanding of chemical processes to make some assumptions about possible reactions, ultimately we must do an experiment to determine the chemical equation. This topic is covered in introductory chemistry textbooks and will be briefly considered here.

Let us return to the reaction between silver nitrate and sodium chloride solutions. We know that in these solutions the various species are present in their ionic form. When we mix the two solutions a precipitate is formed. From our experience with chemical reactions we know that silver halide salts are very insoluble; hence, we might conclude that the precipitate is most likely silver chloride. But in order to be certain we must analyze the precipitate. Our analysis reveals that, on a weight basis, the precipitate is 75.3% silver and 24.7% chlorine. Our original guess is correct—the precipitate is an insoluble silver halide. What is the chemical formula of the precipitate? If we assume that we have 100 g of precipitate (we make this assumption in order to simplify the calculation—the actual value doesn't matter), we can calculate the number of moles of silver and chlorine in the compound.

$$\text{Moles of silver} = (100 \text{ g}) \times 0.753/107.9 \text{ g mol}^{-1} = 0.698 \text{ mol}$$

$$\text{Moles of chlorine} = (100 \text{ g}) \times 0.247/35.45 \text{ g mol}^{-1} = 0.697 \text{ mol}$$

The number of moles of silver and chlorine are essentially identical, and the compound has the formula AgCl. Because neither sodium nor nitrate is found in the precipitate, we will make the assumption that these species remain in solution as spectator ions. The net ionic chemical equation for this precipitation reaction is



The procedure we used to determine the formula of the compound can be summarized as follows:

1. Determine the weight percent of each element in the compound.
2. Using 100 g as a basis, determine the weight of each element in the compound.
3. For each element determine the number of moles by dividing the weight of the element by the gram-atomic weight of the element.
4. Using the element with the least number of moles, determine the relative number of moles of each of the other elements. After rounding, this should yield integer values for each of the elements, and these integers represent the formula for the compound.

EXAMPLE 1-6 During a chemical reaction a precipitate forms that has the following composition (in weight percent): Ca = 39.74, P = 18.42, O = 38.07, and F = 3.77. Determine the formula for this compound.

First convert to absolute weight on the basis of 100 g, and then determine the number of moles of each element.

Element	wt%	wt/100 g	at. wt	Moles
Ca	39.74	39.74	40.08	0.992
P	18.42	18.42	30.97	0.595
O	38.07	38.07	16.00	2.379
F	3.77	3.77	19.00	0.198

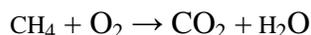
The element present in the smallest amount is fluorine. Dividing each of the other elements by the number of moles of fluorine yields, per mole of fluorine, 12 moles of oxygen, 3 moles of phosphorus, and 5 moles of calcium. The formula for this compound is $\text{Ca}_5\text{P}_3\text{O}_{12}\text{F}$ [or $\text{Ca}_5(\text{PO}_4)_3\text{F}$], the formula for the mineral fluoroapatite.

The formula we calculated in Example 1-6 is the *empirical formula*, i.e., *the formula that represents the simplest whole-number ratio of the atoms that make up the compound*. This formula, however, may not be the correct formula. For example, if you are familiar with organic compounds, you will know that many organic compounds consist of multiple numbers of all elements found in the compound. We can determine the *molecular formula* (*the actual number of each type of atom in the compound*) by comparing the formula weight to the molecular weight of the compound.

EXAMPLE 1-7 The empirical formula of a compound is CH_3 and its molecular weight is 30 g. Calculate the molecular formula for the compound.

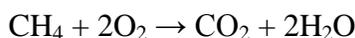
The formula weight is 15 g mol^{-1} ($1\text{C} \times 12 \text{ g mol}^{-1} + 3\text{H} \times 1 \text{ g mol}^{-1}$). The molecular weight is twice the formula weight ($30 \text{ g}/15 \text{ g} = 2$). Thus, the molecular formula of the compound is C_2H_6 .

Based on experiments, we can determine the reactants and products of a chemical reaction. However, simply determining the reactants and products does not completely describe the chemical reaction. We must also balance the number of atoms on each side of the equation. Returning to a previous example involving the combustion of methane, experiments tell us that methane combines with oxygen to produce carbon dioxide and water. The simplest equation that represents this reaction is



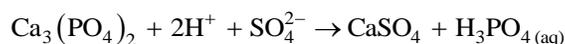
Inspection of this equation reveals that the number of hydrogen and oxygen atoms on each side of the equation is not the same; i.e., the equation is not balanced. To balance the equation, we must add 2 hydrogen atoms to the right side of the equation, giving 2 water molecules. We now

have a deficiency of oxygen atoms on the left side of the equation and we must add 2 oxygen atoms, i.e., increase the number of oxygen molecules to 2. The balanced equation is

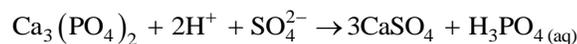


Unfortunately, there are no simple rules for balancing chemical equations. After you have written the equation showing the reactants and products, the balancing of the equation proceeds by inspection. The formulas of the compounds cannot change, so the equation can only be balanced by changing the number of the formula units. It is usually best to start with the most complicated species in the chemical equation and then proceed to the least complicated species. In oxidation reactions, where molecular oxygen and water are involved, these two species are balanced last because they can be added to the reaction in appropriate amounts. A more detailed discussion of the balancing of oxidation-reduction reactions is found in Chapter 4.

EXAMPLE 1–8 In the production of phosphate fertilizer, calcium phosphate rock $[\text{Ca}_3(\text{PO}_4)_2]$ is reacted with sulfuric acid (H_2SO_4) to produce calcium sulfate (CaSO_4) and phosphoric acid (H_3PO_4). Sulfuric acid is a strong acid (i.e., it dissociates completely in water), and phosphoric acid is a weak acid (i.e., it only partly dissociates in water). The chemical reaction can be written as follows:



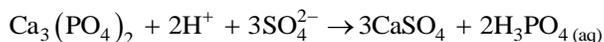
To balance this equation, we will start with the most complicated compound, calcium phosphate. Calcium phosphate contains 3 Ca atoms. Ca atoms are found in the product calcium sulfate. In order to balance the calcium, we need 3 calcium sulfate molecules.



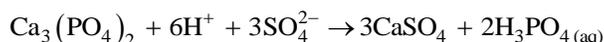
There are now 3 sulfur atoms in the products. We need 3 sulfur atoms in the reactants. Hence, there must be 3 sulfate molecules in the reactants. The equation now becomes



In order to balance the number of phosphorus atoms in the reactants (2), we need 2 phosphorus atoms in the products. The equation becomes



We now have 6 hydrogen atoms in the products, but only 2 in the reactants. To balance the hydrogen atoms, we need to add 4 hydrogen atoms to the left-hand side of the equation, which gives



The only remaining atom is oxygen. As written, there are 20 oxygen atoms in the reactants and 20 oxygen atoms in the products. The equation is now balanced.

GASES

An ideal gas consists of atoms and/or molecules that move completely independently of each other and occupy a volume that is much greater than the total volume of the atoms/molecules; i.e., the actual volume of the atoms/molecules is negligible relative to the total volume. Ideal gases obey two well-known laws that relate pressure and volume (Boyle's law) and temperature and volume (Charles's law). All real gases depart to some extent from ideality.

Experiments carried out on real gases show an inverse relationship between the volume of the gas and the pressure. If the pressure is doubled, the volume decreases by one-half. A plot of volume versus the reciprocal of pressure yields a straight line (Figure 1-6). **Boyle's law** relates the changes in pressure and volume of a gas and can be stated mathematically as

$$PV = k \quad (1-13)$$

where P is pressure (force per unit area), V is volume, and k is a constant. In SI units, pressure is measured in Pascals (Pa) and volume is measured in m^3 . However, atmospheres are often used for pressure and liters are more commonly used for the volume of a gas. The equation of a straight line is

$$y = mx + b \quad (1-14)$$

With reference to Figure 1-6, $y = \text{volume}$, $x = 1/P$, $m = k$, and $b = 0$ (the line intercepts the y -axis at a volume of 0 liters; i.e., at infinite pressure the gas is compressed to zero volume). Note that the slope k corresponds to volume times pressure, and in commonly used units the constant would be expressed in L atm. For an ideal gas, this value is 22.41 L atm. At low pressures, real

gases have constant slopes and k values that are near 22.41 L atm. At higher pressures, real gases do not show a linear relationship between V and $1/P$. However, the deviation with pressure is usually relatively small.

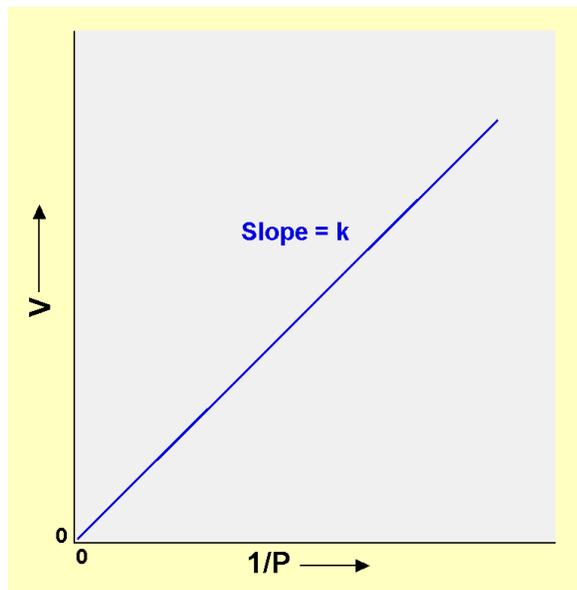


Figure 1-6 A plot of V versus $1/P$ for an ideal gas gives a straight line, and the slope of the line is the Boyle's law constant k .

Experiments carried out on real gases show that there is a direct relationship between the volume of the gas and the temperature. As the temperature of the gas decreases so does the volume. This relationship is known as *Charles's law* and can be stated mathematically as

$$V = bT \quad (1-15)$$

where V is the volume, T is the temperature (in K), and b is a proportionality constant. An interesting result of these experiments is that extrapolation to zero volume for all gases gives a consistent value of -273.15°C . At this temperature, the volume of an ideal gas would be zero. At first glance, this result seems ridiculous (a little bit like the Cheshire cat in *Alice in Wonderland*), because matter cannot contract to zero volume. The key phrase here is "ideal gas." All gases liquify before reaching -273.15°C and therefore clearly do not behave as ideal gases at these low temperatures. The temperature at which the volume of an ideal gas becomes zero is the basis for the absolute (Kelvin) temperature scale: $\text{K} = 0$ corresponds to -273.15°C . The Kelvin and Centigrade degrees are the same size; hence, the Kelvin and Centigrade scales can be

mathematically related as follows:

$$K = ^\circ C + 273.15 \quad (1-16)$$

Note that in the ideal gas law the temperature is given in Kelvin. Because a gas cannot have a negative volume, 0 K has a special significance and is referred to as *absolute zero*. Although absolute zero has never been achieved, a number of clever experiments have been conducted in which temperatures close to 0 K have been obtained.

Avogadro postulated that equal volumes of gases at the same temperature and pressure contain the same number of particles. *Avogadro's law* relates the volume of a gas to the number of moles and can be stated mathematically as

$$V = an \quad (1-17)$$

where V is the volume, n is the number of moles, and a is a proportionality constant.

Boyle's, Charles's, and Avogadro's laws can be combined to form the *ideal gas law*, which is stated mathematically as

$$PV = nRT \quad (1-18)$$

where P is the pressure, V is the volume, n is the number of moles, R is the universal (or ideal) gas constant, and T is the temperature (in K). The value of the universal gas constant depends on the units used to express pressure and volume. For example, if the pressure is in atmospheres and the volume is in liters, $R = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$. The ideal gas law is an equation of state because it defines the condition of the gas at a given time. If any three of the four properties of the gas (pressure, volume, number of moles, and temperature) are known, the fourth can be determined from the ideal gas law. Most gases approximately obey this relationship at pressures less than 1 atm.

EXAMPLE 1-9 A balloon is filled with helium gas. The outside temperature is 20°C, the atmospheric pressure is 1 atm, and the volume of the balloon is 2 L. Calculate the number of moles of helium in the balloon.

From the ideal gas law,

$$n = PV/RT = [(1 \text{ atm})(2 \text{ L})]/[(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(293.15 \text{ K})] = 0.083 \text{ mol}$$

The *volume occupied by 1 mole of a gas* is referred to as the **molar volume**. For an ideal gas at 0°C and 1 atm pressure, the molar volume is 22.42 L. Note that this volume would vary as a function of temperature and pressure. The specific conditions of 0°C and 1 atm are referred to as **standard temperature and pressure (STP)**. Molar volumes at STP for a number of common gases are tabulated in Table 1–5.

Table 1–5 Molar Volumes for Various Gases at STP*

Gas	Molar volume (L)
Oxygen (O ₂)	22.397
Nitrogen (N ₂)	22.402
Hydrogen (H ₂)	22.433
Helium (He)	22.434
Argon (Ar)	22.397
Carbon dioxide (CO ₂)	22.260
Ammonia (NH ₃)	22.079

*From Zumdahl (1989).

EXAMPLE 1–10 Calculate the volume of CO₂ released at STP when 25 g of calcite (CaCO₃) are dissolved in hydrochloric acid. The molecular weight of CaCO₃ is 100.1 g.

$$\text{Moles of CaCO}_3 \text{ dissolved} = 25 \text{ g} / 100.1 \text{ g mol}^{-1} = 0.25 \text{ mol}$$

During this reaction 0.25 mol of CO₂ is released. At STP, the molar volume of CO₂ is 22.260 L mol⁻¹ (Table 1–5).

$$\text{Volume of CO}_2 \text{ released} = (0.25 \text{ mol})(22.260 \text{ L mol}^{-1}) = 5.565 \text{ L}$$

So far, we have considered the behavior of ideal gases. But most gases, particularly at high pressures and low temperatures, deviate from ideal behavior. In fact, experimental studies have shown that real gases most closely approximate ideal gases only at very low pressures and very

high temperatures. There are two major reasons for this deviation from ideality: (1) Gas molecules/atoms do have a finite volume, and when the number of gas molecules/atoms increases (as they would at high pressures), the gas molecules/atoms comprise a significant portion of the volume; and (2) gas molecules/atoms do interact with each other, and as the number of molecules/atoms increases, the number of interactions increases. These deviations were taken into account in a model developed in the late 1800s by van der Waals. Two terms were introduced to the ideal gas equation. The first has the form $V - nb$, where n is the number of moles of gas and b is an empirical constant that depends on the gas. This first term corrects for the volume of the gas molecules/atoms. The second term has the form $a(n/V)^2$, where a is an empirical constant, n is the number of moles, and V is the volume. The second term corrects for the interactions between the gas molecules/atoms. Taking into account these two corrections, the observed pressure is described by the following mathematical relationship:

$$P_{\text{obs}} = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 \quad (1-19)$$

Table 1-6 Van der Waals Constant for Some Common Gases*

Gas	a (atm L ² mol ⁻²)	b (L mol ⁻¹)
He	0.0346	0.0238
Ne	0.208	0.0167
Ar	1.355	0.0320
Xe	4.192	0.0516
Kr	5.193	0.0106
H ₂	0.245	0.0265
N ₂	1.370	0.0387
O ₂	1.382	0.0319
Cl ₂	6.343	0.0542
CO ₂	3.658	0.0429

Gas	a (atm L ² mol ⁻²)	b (L mol ⁻¹)
CH ₄	2.303	0.0431
NH ₃	4.225	0.0371
H ₂ O	5.537	0.0305

*From *CRC Handbook of Chemistry and Physics* (2000).

This equation can be rearranged to give the *van der Waals equation*:

$$\left[P_{\text{obs}} + a \left(\frac{n}{V} \right)^2 \right] (V - nb) = nRT \quad (1-20)$$

Van der Waals constants for some of the common gases are tabulated in Table 1–6.

EXAMPLE 1–11 A cylinder of compressed nitrogen has a volume of 100 L and contains 500 mol of N₂. At a temperature of 25°C, calculate the pressure exerted by the gas on the cylinder.

First solve the van der Waals equation for pressure.

$$P_{\text{obs}} = \frac{nRT}{V - nb} - a \left(\frac{n}{V} \right)^2$$

25°C = 298.15 K. Substituting the appropriate values into the van der Waals equation,

$$P_{\text{obs}} = \frac{(500 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{(100 \text{ L}) - (500 \text{ mol})(0.0387 \text{ L mol}^{-1})} - (1.37 \text{ atm L}^2 \text{ mol}^{-2}) \left(\frac{500 \text{ mol}}{100 \text{ L}} \right)^2 = 117.4 \text{ atm}$$

Gas cylinder pressures are often reported in pounds per square inch (psi); 1 atm = 14.7 lb in⁻². Therefore, for this gas cylinder,

$$P = 117.4 \text{ atm} \times 14.7 \text{ lb in}^{-2} \text{ atm}^{-1} = 1726 \text{ psi}$$

STRUCTURE AND PROPERTIES OF WATER

Water is arguably the most important substance on earth, and without water, life as we know it would not exist. Compared to other liquids, water has a number of unique properties. These are

summarized in Table 1–7.

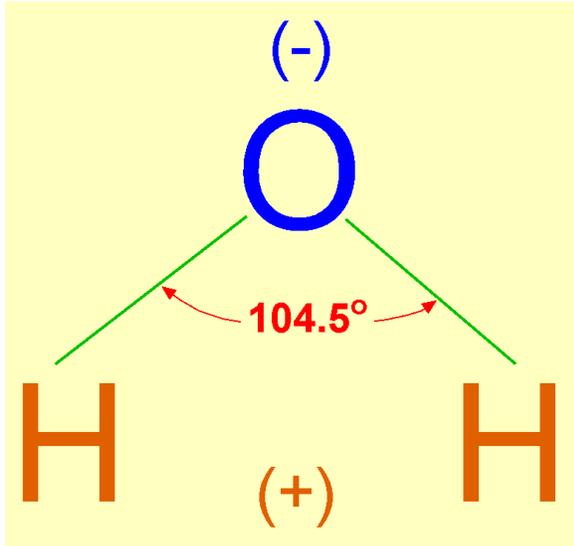


Figure 1–7 Structure of the water molecule. Water behaves as a polar molecule.

Table 1-7 Properties of Water*

Property	Comparison to other substances
Heat capacity	Highest of all common liquids (except ammonia) and solids
Latent heat of fusion	Highest of all common liquids (except ammonia) and most solids
Latent heat of vaporization	Highest of all common substances
Dissolving ability	Dissolves more substances (particularly ionic compounds), and in greater quantity than any other common liquid
Transparency	Relatively high for visible light
Physical state	The only substance that occurs naturally in all three states at the earth's surface
Surface tension	Highest of all common liquids
Conduction of heat	Highest of all common liquids (Hg is higher)
Viscosity	Relatively low viscosity for a liquid

* Adapted from Sverdrup et al. (1942).

These unique properties are due to the structure of the water molecule (Figure 1-7). The structure of nonmetallic molecules can be described using the *valence shell electron-pair repulsion (VSEPR) model*, which is described in introductory chemistry textbooks. This model assumes that the molecular structure is determined principally by the minimization of electron-pair repulsions. There are eight valence electrons involved in the water molecule. Six electrons are associated with oxygen and one electron is associated with each of the hydrogens. Electrons exist in pairs. Two pairs are shared between the oxygen and two hydrogens. The other two pairs are nonbonding and are sometimes referred to as *lone pairs*. In order to minimize the electron-pair interactions, the pairs are arranged in a tetrahedral configuration around the oxygen so that the angle between pairs is 109.5° . We see from Figure 1-7 that this angle is somewhat smaller for the water molecule. This is usually explained by assuming that the lone pairs need more space around the oxygen atom than do bonding pairs. From the structure of the water molecule it is apparent that water is a polar molecule (Figure 1-7), and this is the key factor in determining the physical and chemical properties of water. For example, ionic compounds dissolve readily in water because of the polarity of the water molecule. Conversely, covalently bonded compounds are relatively insoluble in water. The hydrogen bonding between water molecules is also responsible for the high latent heats of vaporization (539 cal g^{-1}) and fusion (80 cal g^{-1}). The heat of vaporization varies as a function of temperature and can be calculated using the following equation:

$$L = 596 \text{ cal g}^{-1} - [(0.56 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}) \times T (\text{ }^\circ\text{C})] \quad (1-21)$$

Water also has one of the highest heat capacities of any common substance. *Heat capacity* is the *amount of heat energy needed to raise the temperature of 1 g of a substance 1°C* . For water, the heat capacity is $1 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$.

As noted, water can exist in all three states at the earth's surface. In the vapor state, water exists as separate molecules that move freely past each other. In the liquid state, water is a mixture of clusters of water molecules (many forming six-sided rings) and single water molecules (Figure 1-8b). In the solid state, water molecules form a network of six-sided rings (Figure 1-8a). These variations in the structure of water are responsible for water behaving unlike almost any other substance in terms of density variations. For virtually all substances, the solid

state is denser than the liquid state. However, in the case of water, the solid state is less dense. This is because the six-sided ring structures occupy a greater volume than the individual water molecules and clusters of molecules found in the liquid state (Figure 1-8).

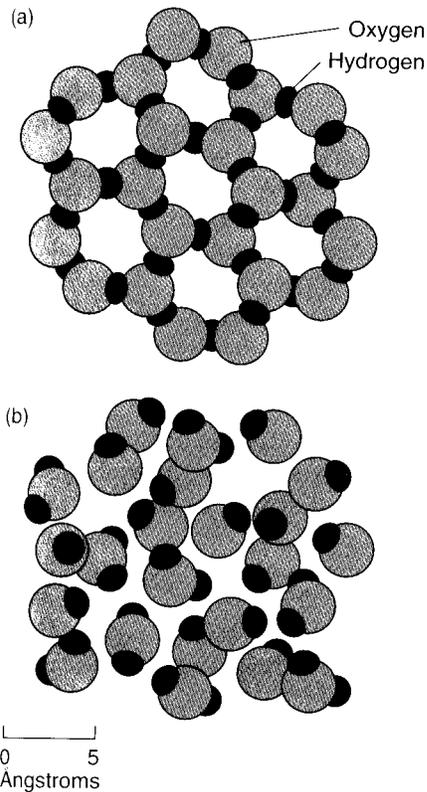


Figure 1-8 (a) The crystal structure of ice showing the six-sided rings formed by 24 water molecules, (b) The structure of liquid water. In the same volume of liquid water, there are 27 water molecules; hence, liquid water has a greater density than ice. From Gross and Gross (1996).

Another unique characteristic of water is that its temperature of maximum density is above the freezing point (Figure 1-9). As the temperature of water decreases the molecular motion of the molecules decreases, so they tend to be closer together (i.e., the number of water molecules per unit volume increases). At the same time, the water molecules are forming clusters and six-sided rings that occupy a greater volume than the same number of single water molecules. The increase in volume caused by this ordering eventually becomes more important than the decrease in volume due to the decreasing molecular motion. The crossover point represents the

temperature of maximum density ($\sim 4^\circ\text{C}$ for freshwater). The freezing-point temperature, and the temperature of maximum density, decrease as the salt content of water increases (Figure 1-10). This becomes an important factor in the oceans. Salinity (defined in Chapter 10) is a measure of the salt content of seawater. Average salinity for seawater is $\sim 35\text{‰}$. With reference to Figure 1-10, seawater is densest at the freezing-point temperature, unlike the situation for freshwater. These differences in the freezing-point temperature, and temperature of maximum density, play an important role in the circulation of freshwater and seawater bodies, the formation of sea ice, and other processes. The interested student can learn more about this topic in a standard reference on oceanography.

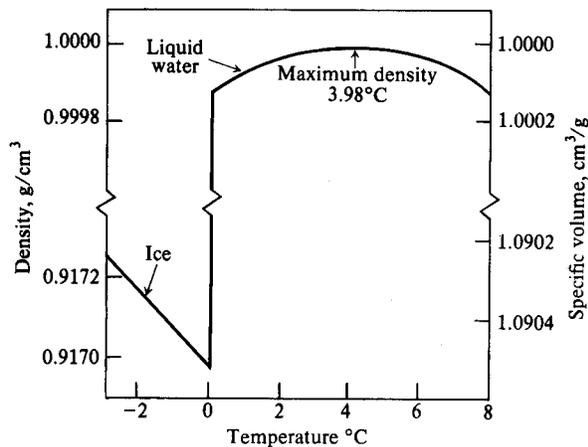


Figure 1-9 Density of pure water near the freezing point. From Duxbury (1971).

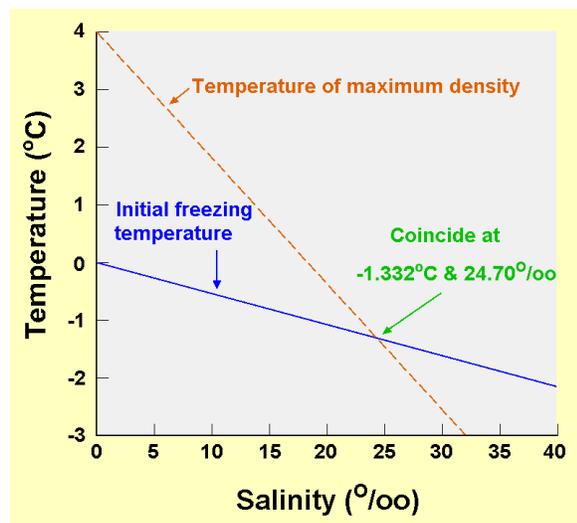


Figure 1-10 Relationship between salinity, decrease in freezing-point temperature, and

temperature of maximum density. After Duxbury (1971).

BOX MODELS AND GEOCHEMICAL CYCLES

Box models and the steady-state assumption are widely used in the environmental sciences to trace the passage of various constituents through the bio-geo-hydro-atmospheres and to assess the impact of anthropogenic inputs on these natural cycles. A *box model* consists of several boxes showing the reservoirs for a particular substance and the rate at which material is transferred between the reservoirs. Fluxes between these reservoirs are generally indicated by arrows. In a *steady-state system*, the total amount of a substance in each reservoir remains constant; thus the rate of addition to, and removal of a material from a reservoir must be the same. In a pioneering work, Garrels et al. (1975) used box models to describe geochemical cycles for a number of elements of environmental interest.

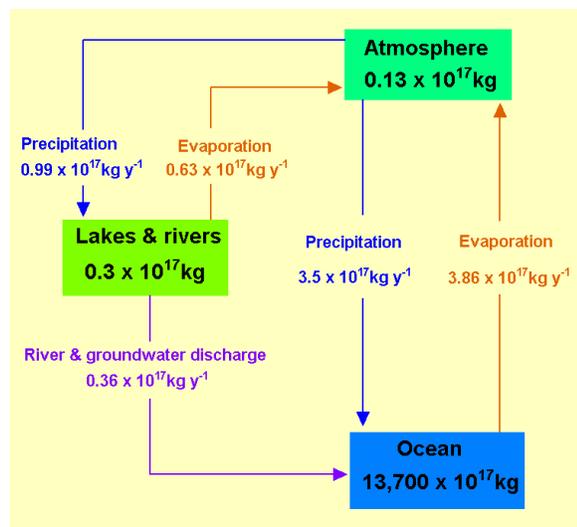


Figure 1–11 Simplified box model of the hydrologic cycle. Modified from Drever (1997).

A very simple box model for the hydro-logic cycle is shown in Figure 1–11. Using the data from this figure, we can calculate the residence time for water in the various reservoirs. *Residence time* is defined as *the average length of time a particular substance will reside in a reservoir*. The mathematical expression is

$$\text{Residence Time} = \frac{\text{Amt. of material in reservoir}}{\text{Rate of addition (removal)}} \quad (1-22)$$

EXAMPLE 1-12 Calculate the residence time for water in the atmospheric reservoir.

Because this is a steady-state model, the rate of addition of water to the reservoir must equal the rate of removal. We can use either set of fluxes. Using the rate of addition, 0.63×10^{17} kg of water are added each year by evaporation from lakes and rivers and 3.86×10^{17} kg are added each year by evaporation from the ocean. The total rate of addition is 4.49×10^{17} kg y^{-1} . The residence time for water in the atmospheric reservoir is

$$\begin{aligned}\text{Residence Time} &= \frac{\text{Amt. of material in reservoir}}{\text{Rate of addition}} = \frac{0.13 \times 10^{17} \text{ kg}}{4.49 \times 10^{17} \text{ kg y}^{-1}} \\ &= 0.029 \text{ y} = 10.6 \text{ d}\end{aligned}$$

The residence time of water vapor in the atmospheric reservoir is very short. This result suggests that changes in the rate of addition of water to the atmosphere (e.g., increases in the rate of evaporation due to atmospheric warming) would lead to rapid increases in water vapor in the atmosphere and a corresponding increase in the amount of precipitation. This is sometimes referred to as the *speeding up of the hydrologic cycle* due to atmospheric warming.

What happens when we perturb a steady-state system? This problem can be investigated in several ways. The approach illustrated here is a ***first-order kinetics model***. In Chapter 2, we will discuss kinetics at some length and present equations that describe various reaction orders. One of the most common types of reactions is a first-order reaction, an example of which is radioactive decay. In terms of geochemical cycles, we can write the following first-order kinetics equation:

$$dA_i/dt = F_{\text{input}} - F_{\text{output}} = F_{\text{input}} - k A_i \quad (1-23)$$

where dA_i/dt is the rate of change of the amount of substance A in reservoir i , F_{input} is the rate of addition of substance A to the reservoir, F_{output} is the rate of removal of substance A from the reservoir, and k is the rate constant. When the system is in a steady state, $F_{\text{input}} = F_{\text{output}}$. Solving equation 1-23 for the amount of substance A in reservoir i at some particular time gives

$$A_i(t) = \frac{F_{\text{input}}}{k} - \left(\frac{F_{\text{input}}}{k} - A_i^0 \right) \exp(-kt) \quad (1-24)$$

where A_i^0 is the amount of substance A in the reservoir at time zero. When the system is in a steady state, equation 1-23 can be written

$$dA_i / dt = 0 = F_{input} - kA_i^0 \quad (1-25)$$

and

$$k = F_{input} / A_i^0 \quad (1-26)$$

Note that in this model the new steady state for a particular reservoir is approached exponentially.

EXAMPLE 1–13 Garrels et al. (1975) present a box model for the prehuman mercury cycle. This model is shown in Figure 1-12. The vast majority of the mercury is contained in the sediments and is very slowly released to the land reservoir by erosion. The small amount of mercury vapor in the atmospheric reservoir suggests that changes in the mercury flux to this reservoir could substantially affect the concentration of mercury in the atmosphere. Garrels et al. (1975) considered the impact of mining, which greatly accelerates the rate at which mercury is transferred from the sediments to the land. Mining results in a $90 \times 10^8 \text{ g y}^{-1}$ increase in the flux of mercury to the land reservoir. Emission of mercury vapor to the atmosphere due to anthropogenic activities was estimated to be $102 \times 10^8 \text{ g y}^{-1}$. The other fluxes also increased.

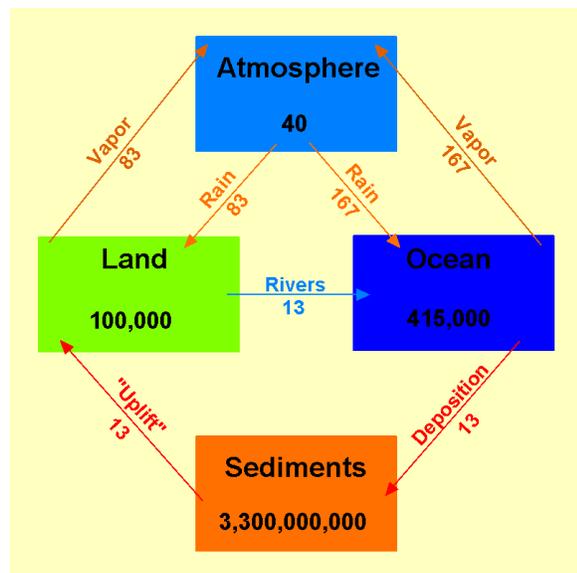


Figure 1–12 Prehuman cycle for mercury. Reservoir masses in units of 10^8 g . Fluxes in units of

10^8 g y^{-1} . From Garrels et al. (1975).

Let us evaluate the impact of the anthropogenic mercury vapor emissions on the mercury content of the atmosphere using the first-order kinetic model. First we calculate the rate constant using equation 1–26 and the steady-state model shown in Figure 1–12. In the prehuman mercury cycle, the total input of mercury vapor to the atmospheric reservoir is $250 \times 10^8 \text{ g y}^{-1}$.

$$k = F_{\text{input}}/A_i^0 = 250 \times 10^8 \text{ g y}^{-1} / 40 \times 10^8 \text{ g} = 6.25 \text{ y}^{-1}$$

Adding the anthropogenic mercury vapor input of $102 \times 10^8 \text{ g y}^{-1}$ to the prehuman input gives $F_{\text{input}} = 352 \times 10^8 \text{ g y}^{-1}$. We can now evaluate equation 1–24 for any time t . For example, when $t = 1$ year,

$$\begin{aligned} A_i(t) &= \frac{F_{\text{input}}}{k} - \left(\frac{F_{\text{input}}}{k} - A_i^0 \right) \exp(-kt) = \frac{352}{6.25} - \left(\frac{352}{6.25} - 40 \right) \exp[(-6.25)(1)] \\ &= 56.29 \times 10^8 \text{ g} \end{aligned}$$

We see that after 1 year the mercury content of the atmosphere has increased by 41%. Are we near the final steady-state value for the atmosphere? Because this is an exponential relationship, the approach to the new equilibrium will be asymptotic. We can easily solve equation 1–24 for multiple time intervals using a spreadsheet. Such a solution is shown in Figure 1-13. From the steady-state model shown in Figure 1-12, we know that the mean residence time for mercury in the atmospheric reservoir is 0.16 year. Given this short mean residence time, we would expect that the atmosphere would quickly achieve a new steady state. From Figure 1-13, we see that the atmosphere has effectively reached its new equilibrium value after 1 year. Note that in doing these calculations we have assumed the rate constant calculated from the steady-state model remains constant when the system is perturbed. This is not necessarily true, and calculations of this type need to be evaluated in terms of the actual behavior of the system.

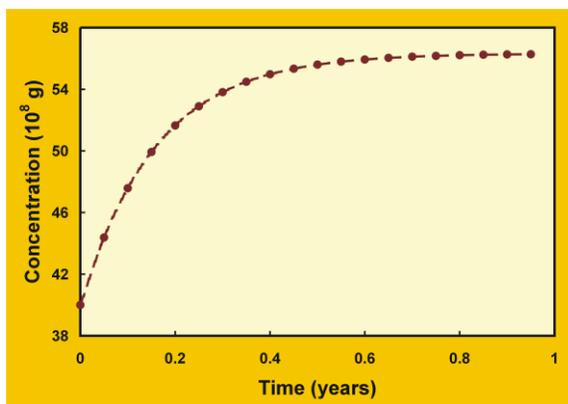


Figure 1–13 Variation in mercury content of the atmosphere as a function of time.

Another important factor in developing and using steady-state models is time. Perhaps the clearest distinction can be made between short-term and long-term cycles. This is illustrated using carbon. In the short-term carbon cycle (Figure 1–14a), the processes are biological and rapid physicochemical processes, such as gas exchange. The time scales are on the order of days to years. These types of cycles are easily disrupted by anthropogenic changes—in the case of carbon by the release of CO₂ by the burning of fossil fuels and deforestation—and are, hence, of significant environmental interest. In the long-term carbon cycle, the processes are largely geological and operate on the time scale of hundreds of thousands to millions of years. The long-term cycle for carbon is illustrated in Figure 1–14b.

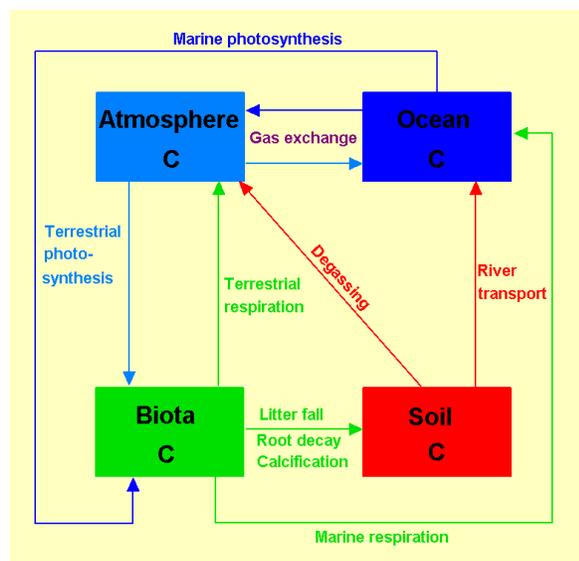


Figure 1–14^a The short-term carbon cycle, excluding anthropogenic inputs. After Berner (1999).

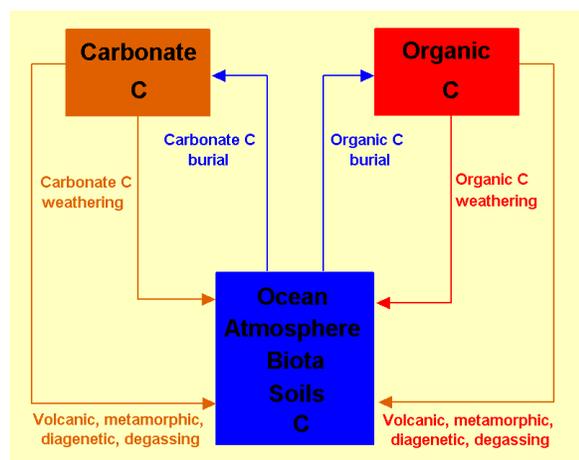


Figure 1–14b The long-term carbon cycle. After Berner (1999).

In a sense, the traditional steady-state box models are static; i.e., they do not show the various cause-and-effect feedbacks that can occur between the different reservoirs. Berner (1999) proposed a different approach using an interactive model that shows the various cause-and-effect feedbacks. This type of model (a cause-and-effect feedback model), for the long-term carbon cycle, is shown in Figure 1-15. In this model, the long-term carbon cycle consists of two subcycles—silicate-carbonate and organic. In the silicate-carbonate subcycle, atmospheric CO_2 is used in the weathering of Ca and Mg silicate minerals, the Ca and Mg ions are removed from solution as carbonate minerals, and the CO_2 is ultimately returned to the atmosphere by the thermal breakdown of carbonates. The organic subcycle involves the sequestering of carbon by the burial of organic matter in sediments and the subsequent release of carbon during weathering by oxidation of organic matter in old sediments. Note that both of these subcycles are largely geological in character.

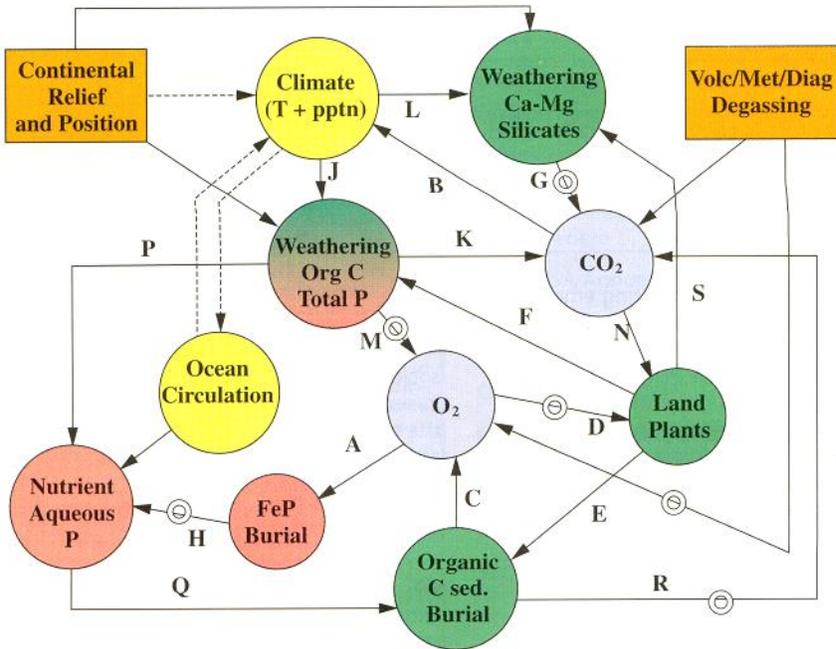


Figure 1–15 Cause-and-effect feedback diagram for the long-term carbon cycle. Arrows originate at causes and end at effects. Arrows with small concentric circles represent inverse responses; arrows without concentric circles represent direct responses. From Berner (1999).

On the cause-and-effect feedback diagram (Figure 1–15), the arrows originate at causes and end at effects. Arrows with small concentric circles indicate inverse responses; those without small concentric circles indicate direct responses. For example, the arrow labeled M shows the cause-and-effect relationship between the weathering of organic carbon and atmospheric oxygen. In this case, the weathering of organic carbon leads to a decrease in atmospheric oxygen, an inverse response as indicated by the small concentric circles on the arrow. The arrow labeled L shows the cause-and-effect relationship between climate and the weathering of Ca-Mg silicates. An increase in temperature and/or precipitation leads to an increase in the rate of weathering, a direct response as indicated by the absence of small concentric circles on this arrow.

We can also look at subcycles in this diagram to see if they have positive or negative feedbacks. If the subcycle contains an even number of concentric circles, the feedback is positive. If the subcycle contains an odd number of concentric circles, the feedback is negative. Positive feedbacks lead to an amplification of an initial increase or decrease, and negative feedbacks lead to a dampening of the initial increase or decrease. For example, consider the

subcycle B-L-G, which has an odd number of concentric circles. In this cycle, increasing CO_2 leads to a warmer and wetter climate with a concomitant increase in the weathering of Ca-Mg silicates. This increase in weathering leads to an increase in the uptake of CO_2 , a negative feedback. Thus, this cycle tends to dampen increases in CO_2 . The subcycle B-J-K contains no concentric circles (by default, an even number). In this cycle, an increase in CO_2 leads to a warmer and wetter climate and increased weathering of organic carbon, releasing CO_2 to the atmosphere, a positive feedback loop. Conversely, a decrease in CO_2 would lead to a cooler and drier climate and a decrease in the weathering of organic carbon, decreasing the amount of CO_2 released to the atmosphere. This is also a positive feedback, because it reinforces the original change, which was a decrease in atmospheric CO_2 .

QUESTIONS AND PROBLEMS

1. Distinguish between the *continuous* and *discontinuous* view of matter.
2. What is a *photon*?
3. Distinguish between the *principal*, *azimuthal*, *magnetic*, and *spin* quantum numbers.
4. What is the *Pauli exclusion principle*, and what is its significance?
5. What is the *Heisenberg uncertainty principle*, and what is its significance?
6. Why are the *5s* orbitals filled before the *4d* orbitals?
7. Define *valence*.
8. With reference to Appendix I, explain why the rare earth elements (La–Lu) usually have a valence of +3.
9. Why are the elements Sc–Zn sometimes referred to as the transition elements?
10. Distinguish between *cations* and *anions*.
11. Distinguish between, and explain, *emission* and *absorption spectra*.
12. Define *isotope*.
13. What is the *strong force*?
14. Name and describe the four types of chemical bonding.

15. Define *molarity*, *molality*, and *normality*.
16. What are *precipitation*, *acid–base*, and *oxidation-reduction* reactions?
17. Distinguish between an *empirical* and a *molecular formula*.
18. Define and discuss *Boyle's* and *Charles's laws*.
19. What is the significance of *absolute zero*? Describe the experiment that led to the initial concept and estimate of the temperature of absolute zero.
20. Describe the structure of water, and explain why this structure is responsible for many of the unique properties of water, such as its high heat capacity, high latent heats of fusion and vaporization, and the rather remarkable observation that solid water is less dense than liquid water.
21. When we make ice cream, we pack a mixture of ice and salt around the container of ice cream mix. Why do we do this?
22. What do we mean when we say a system is in a *steady state*?
23. Distinguish between short-term and long-term geochemical cycles. What is the key factor used to make this distinction?
24. How does a cause-and-effect feedback model differ from a steady-state box model?
25. For the Bohr atom, calculate the energy that is released when an electron moves from the fourth allowed orbit to the second allowed orbit. Calculate the wavelength of the emitted radiation.
26. Calculate the wavelength of an electron in the third orbit of the Bohr atom.
27. Given the principal quantum number $n = 3$, how many electrons can be accommodated in the various orbitals? Write the complete set of quantum numbers.
28. Given the principal quantum number, $n = 4$, how many electrons can be accommodated in the various orbitals? Write the complete set of quantum numbers.
29. Write the electron formula for a neutral atom having 16 electrons. Predict the possible valences for this atom.

30. Write the electron formula for a neutral atom having 51 electrons. Predict the possible valences for this atom.

31. ${}_{26}^{57}\text{Fe}$ contains how many protons? how many neutrons?

32. ${}_{51}^{121}\text{Sb}$ contains how many protons? how many neutrons?

33. There are three stable isotopes of neon.

a. Using the following data, calculate the atomic weight of neon.

Isotope	% Abundance	Mass (amu)
${}^{20}\text{Ne}$	90.48	19.99244
${}^{21}\text{Ne}$	0.27	20.99385
${}^{22}\text{Ne}$	9.25	21.99139

b. If 5.4 mol of neon gas are present in a gas cylinder, calculate the weight of neon gas in the cylinder.

c. Calculate the number of neon atoms in the gas cylinder.

d. Calculate the mass (in g) of a single neon atom.

34. There are five stable isotopes of Ti.

a. Using the following data, calculate the atomic weight of Ti.

Isotope	% Abundance	Mass (amu)
${}^{46}\text{Ti}$	8.0	45.95263
${}^{47}\text{Ti}$	7.28	46.95176
${}^{48}\text{Ti}$	73.8	47.94795
${}^{49}\text{Ti}$	5.5	48.94787
${}^{50}\text{Ti}$	5.4	49.94479

- b.** The chemical formula for the mineral rutile is TiO_2 . Calculate the number of grams of Ti in 45.3 g of rutile.
- c.** Calculate the number of moles of Ti in the rutile.
- d.** Calculate the number of Ti atoms in the rutile.
- e.** Calculate the mass (in kg) of a single Ti atom.
- 35.** The $^{51}\text{V}/^{12}\text{C}$ ratio = 4.2453. Calculate the mass (in amu) of ^{51}V .
- 36.** Calculate the molecular weight of kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$.
- 37.** 1.25 g of NaCl is dissolved in a 1-L solution. Calculate
- a.** The number of moles of NaCl dissolved in the solution.
- b.** The molarity of the NaCl solution.
- c.** The number of Na^+ ions in the solution.
- 38.** 0.02 g of SrSO_4 is dissolved in a 1-L solution. Calculate
- a.** The number of moles of SrSO_4 dissolved in the solution.
- b.** The molarity of the SrSO_4 solution.
- c.** The number of Sr^{2+} ions in solution.
- 39.** A 1-L solution contains 2.2×10^{-4} mol of CaCO_3 . Calculate the mass of CaCO_3 dissolved in the solution.
- 40.** A CaCO_3 - MgCO_3 solid solution contains 3 wt% Mg. Calculate the mole fraction of MgCO_3 in the solid solution.
- 41.** A $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFeSi}_2\text{O}_6$ solid solution (Ca-rich pyroxene) contains 5 wt% Fe. Calculate the mole fraction of $\text{CaMgSi}_2\text{O}_6$ in the solid solution.
- 42.** If you have read the book *Civil Action* you know that the organic chemical TCE played an important role in this famous environmental case. An analysis of TCE reveals that it consists of 18.283 wt% C, 0.767 wt% H, and 80.950 wt% Cl. The molecular weight of TCE is 131.389 g.

- a. Determine the empirical formula for TCE.
- b. Determine the molecular formula for TCE.
43. A chemical analysis of a clay mineral reveals that it consists of 20.903 wt% Al, 21.759 wt% Si, 55.776 wt% O, and 1.562 wt% H. The molecular weight of the clay mineral is 258.16 g.
- a. Determine the empirical formula for this clay mineral.
- b. Determine the molecular formula for this clay mineral.
44. A chemical analysis of a carbon compound gives 82.659 wt% C and 17.341 wt% H. The molecular weight of the carbon compound is 58.123 g.
- a. Determine the empirical formula for this organic compound.
- b. Determine the molecular formula for this organic compound.
45. Balance the following chemical reactions:
- a. $\text{Al}(\text{OH})_3 \text{ gibbsite} + \text{H}^+ \rightarrow \text{Al}^{3+} + \text{H}_2\text{O}$
- b. $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \text{ kaolinite} + \text{H}^+ \rightarrow \text{Al}^{3+} + \text{H}_4\text{SiO}_4(\text{aq}) + \text{H}_2\text{O}$
- c. $\text{CaAl}_2\text{Si}_2\text{O}_8 \text{ anorthite} + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{Al}^{3+} + \text{H}_4\text{SiO}_4(\text{aq})$
- d. $\text{FeOOH} \text{ goethite} + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}$
- e. $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 \text{ jarosite} + \text{H}^+ \rightarrow \text{K}^+ + \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{H}_2\text{O}$
- f. $\text{KAlSi}_3\text{O}_8 \text{ feldspar} + \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{K}^+ + \text{Al}^{3+} + \text{H}_4\text{SiO}_4(\text{aq})$
- g. $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O} \text{ hydromagnesite} + \text{H}^+ \rightarrow \text{Mg}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O}$
- h. $\text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4(\text{aq})$
- i. $\text{As}_2\text{S}_3 \text{ orpiment} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{AsO}_3(\text{aq}) + \text{HS}^- + \text{H}^+$
- j. $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2 \text{ azurite} + \text{H}^+ \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O} + \text{HCO}_3^-$
46. The German airship *Hindenberg*, filled with hydrogen gas, met an unhappy and dramatic fate at Lakehurst Naval Air Station in New Jersey. Assume that the volume occupied by

hydrogen gas was 6×10^7 L, pressure = 1 atm, and temperature = 25°C. Calculate the number of moles of hydrogen gas in the *Hindenberg*. Use the ideal gas equation to solve this problem.

- 47.** The partial pressure of CO₂ gas in a classroom is 0.00036 atm. Partial pressure is the pressure that would be due to CO₂ alone, and partial pressures are often used to express the concentrations of gases. The size of the classroom is 15 m × 6 m × 3 m. Remember that 1 L = 1000 cm³. The classroom temperature is 25°C. Calculate the number of CO₂ molecules in the classroom. Use the van der Waals equation to solve this problem. We will assume that the only interactions are between CO₂ molecules (obviously not true, but we want to give you a fighting chance to solve the problem). At first glance, the algebraic manipulation appears daunting. However, the clever student will recognize that this problem can be set up on a spreadsheet and quickly solved by successive approximations.
- 48.** Calculate the latent heat of vaporization of water at 20°C.
- 49.** With reference to Figure 1–11, calculate
- The residence time of H₂O in the ocean reservoir.
 - The residence time of H₂O in the lakes and rivers reservoir.
 - Comment on the relative residence times of H₂O in all three reservoirs in terms of which would be most affected by changes in the rate of H₂O addition and removal, and which would be least affected. Why?
- 50.** One predicted consequence of greenhouse warming is a speeding up of the hydrologic cycle. With reference to Figure 1–11, suppose greenhouse warming led to a 10% increase in the rate of evaporation of water from lakes, rivers, and the ocean. Calculate the new steady-state value for water in the atmospheric reservoir using a first-order kinetics model. Select an appropriate time for this calculation based on the residence time of water vapor in the atmosphere.
- 51.** Using the cause-and-effect feedback diagram for carbon (Figure 1-15), for each of the following determine if they are positive or negative feedback cycles. What criteria did you use to decide if they were positive or negative feedback cycles? Describe in words

what happens within each cycle.

a. N-S-G

b. A-H-Q-C

c. D-E-C

d. D-F-P-Q-C

e. D-F-M

f. B-J-P-Q-R