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Background and Basic Chemical Principles: Elements, Ions, Bonding, Reactions

1.1 AN OVERVIEW OF ENVIRONMENTAL GEOCHEMISTRY – HISTORY, SCOPE, QUESTIONS, APPROACHES, CHALLENGES FOR THE FUTURE

> The best way to have a good idea is to have a lot of ideas. (Linus Pauling)
>
> All my life through, the new sights of nature made me rejoice like a child. (Marie Curie)
>
> I must speak of the soil hiding the rocks, of the lasting river destroyed by time. (Pablo Neruda)

Environmental and low-temperature geochemistry encompasses research at the intersection of geology, environmental studies, chemistry, and biology, and at its most basic level is designed to answer questions about the behavior of natural and anthropogenic substances at or near the surface of earth. The scope includes topics as diverse as trace metal pollution, soil formation, acid rain, sequestration of atmospheric carbon, and pathways of human–plant–wildlife exposure to contaminants. Most problems in environmental geochemistry require understanding of the relationships among aqueous solutions, geological processes, minerals, organic compounds, gases, thermodynamics and kinetics, and microbial influences, to name a few.

A good example to lay out some of the basic considerations in environmental and low-temperature geochemistry is the fate and transport of lead (Pb) in the environment. In many regions of the Earth, Pb in the earth surface environment is (was) derived from combustion of leaded gasoline, because even in places where it has been banned (most of the world), Pb tends to persist in soil. The original distribution of Pb was controlled at least in part by atmospheric processes ranging from advection (i.e. wind) to condensation and precipitation.

Once deposited on Earth's surface, the fate and transport of Pb is controlled by interactions and relationships among lead atoms, solids compounds (e.g. inorganic minerals or organic matter), plants or other organisms, and the composition of water in soils, lakes, or streams (including dissolved ions like Cl^- and CO_3^{2-} and gases like O_2 and CO_2). In cases where Pb falls on soils bearing the carbonate anion (CO_3^{2-}), the formation of lead carbonate ($PbCO_3$) can result in sequestration of lead in a solid state where it is largely unavailable for uptake by organisms. If the $PbCO_3$ is thermodynamically stable, the lead can remain sequestered (i.e. in a solid state and relatively inert), but changes in chemical regime can destabilize carbonates. For example, acidic precipitation that lowers the pH of soil can cause dissolution of $PbCO_3$, but how much of the carbonate will dissolve? How rapidly? Much like the melting of snow on a spring day, geochemical processes are kinetically controlled (some more than others), so even in cases where phases exist out of equilibrium with their surroundings, we must know something about rate laws in order to predict how fast reactions (e.g. dissolution of $PbCO_3$) will occur.

If Pb is dissolved into an aqueous form (e.g. Pb^{2+}), additional questions of fate and transport must be addressed – will it remain in solution, thus facilitating

Environmental and Low-Temperature Geochemistry, Second Edition. Peter Ryan.

Focus Box 1.1

Defining "Low-Temperature"

In the world of geochemistry and mineralogy, "low-temperature" environments generally refer to those at or near the Earth's surface, whereas "high-temperature" environments include those deeper in the crust, i.e. igneous and metamorphic systems. Most geochemists consider tropical soils with mean annual temperature of 25 °C, alpine or polar systems with mean annual temperature of <5 °C, and sediments buried 1 km below the surface with a temperature of 50 °C, all as low-temperature systems.

Focus Box 1.2

Lead (Pb) and Environmental Justice

Humans have known for thousands of years that lead is toxic, dating back at least to the Roman Empire, but it remains problematic because it relatively abundant and easy to work (e.g. to make pipes for water systems, or as an additive to paint or fuel). A recent case that highlights the connection of geochemistry and human health is that of Flint, Michigan (USA), where lead-bearing pipes were installed as part of the public water supply system in the early twentieth century. Beginning in 2014, a change in public water source from Lake Huron to the Flint River – and in part, the higher amounts of chloride anion (Cl^-) in Flint River water – began to leach lead from the old lead-bearing water mains (pipes) and fittings (Hanna-Attisha et al. 2016). Evidence for the corrosion was obvious to residents in the form of brownish particulates that clouded their water and made it taste bad, but slow response from government resulted in exposure via ingestion. Lead is one of those elements that is harmful at any level, especially to the cognitive development of children. The crisis in Flint serves as one of many examples of environmental injustice (see "environmental (in)justice" in the index for more examples).

uptake by plants? Or will it be carried in solution into a nearby surface water body, where it could be consumed by a fish or amphibian? Or will other soil solids play a role in its fate? Will it become adsorbed to the surface of a silicate clay or organic matter, transported downstream until it ultimately desorbs in lake sediments? We also need to consider the possibility that the $PbCO_3$ does not dissolve, but rather is physically eroded as a particulate (grain) into a stream or lake, where it might dissolve or remain a solid, possibly becoming consumed by a bottom feeder, from which point it could biomagnify up the food chain.

Environmental geochemistry has its origins in groundbreaking advances in chemistry and geology ushered in by the scientific breakthroughs of the late nineteenth and early twentieth centuries, particularly advances in instrumental analysis. The Norwegian Victor M. Goldschmidt is considered by many to be the founder of geochemistry, a reputation earned by his pioneering studies of mineral structures and compositions by X-ray diffraction and optical spectrograph studies. These studies led Goldschmidt to recognize the importance and prevalence of isomorphous substitution in crystals, a process where ions of similar radii and charges can substitute for each other in crystal lattices.

Goldschmidt's peer, the Russian Vladimir I. Vernadsky, had come to realize that minerals form as the result of chemical reactions, and furthermore that reactions at the Earth's surface are strongly mediated by biological processes. The orientation of geochemistry applied to environmental analysis mainly arose in the 1960s and 1970s with growing concern about contamination of water, air, and soil. The early 1960s saw publication of Rachel Carson's *Silent Spring*, and early research on acid rain at Hubbard Brook in New England (F.H. Bormann, G.E. Likens, N.M. Johnson, and R.S. Pierce) emphasized the interdisciplinary thinking required for problems that spanned atmospheric, hydrologic, soil, biotic, and geologic realms.

Current research in environmental geochemistry encompasses problems ranging from nanometer and micron scale (e.g. interactions between minerals and bacteria or X-ray absorption analysis of trace metal speciation), local scale (e.g. acid mine drainage, leaking fuel tanks, groundwater composition, behavior of minerals in nuclear waste repositories) to regional (acid rain, mercury deposition, dating of glacier retreat and advance) and global (climate change, ocean chemistry, ozone depletion) scale. Modern environmental geochemistry employs analytical approaches ranging from field mapping and spatial analysis to spectrometry and diffraction, geochemistry of radioactive and stable isotopes, and analysis of organic compounds and toxic trace metals. While the explosion of activity in this field makes it impossible to present all developments and to acknowledge the research of all investigators, numerous published articles are cited and highlighted throughout the text, and two case studies that integrate many concepts are presented in Appendices I and II.

1.2 THE NATURALLY OCCURRING ELEMENTS – ORIGINS AND ABUNDANCES

The chemical elements on Earth have been around for billions of years, thanks to nucleosynthesis, the Big Bang, approximately 12–15 billion years ago (especially the lighter elements), and processes in the interiors of stars later in the evolution of the universe (heavier elements). The early universe was extremely hot (billions of degrees) and for the first few seconds was comprised only of matter in its most basic form, quarks.

1.2.1 Origin of the light elements H and He (and Li)

Approximately 15 seconds after the Big Bang, the atomic building blocks known as neutrons, protons, electrons, positrons, photons, and neutrinos began to form from quarks, and within minutes after the Big Bang, the first actual atoms formed. Protons combined with neutrons and electrons to form hydrogen ($^1_1$H) and its isotope deuterium ($^2_1$H, or D), which rapidly began to form helium (He) through fusion, a process in which the nuclei of smaller atoms are joined to create larger, heavier atoms: 2H → He + energy, or to be more precise:

$$^1_1\mathrm{H} + ^2_1\mathrm{H} = ^3_2\mathrm{He} + \gamma + \mathrm{E} \tag{1.1}$$

where γ is the symbol for gamma radiation emitted during nuclear fusion. (Note: basic principles of atomic theory are presented in Section 1.3.)

Small amounts of lithium were probably also produced in the first few minutes or hours after the Big Bang, also by fusion (in a simple sense represented as H + He = Li). From a graph of the abundances of elements in the universe (Figure 1.1), it is clear that H and He are the most abundant, and that, for the most part, element abundance decreases exponentially with increasing atomic number

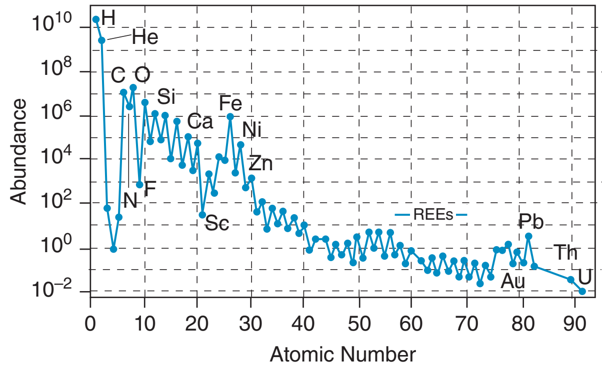

Fig. 1.1 Abundance of elements in the solar system normalized to Si = 10^6 on molar basis with a logarithmic y-axis – this is a standard means of plotting values for this type of data set. Selected elements plus the rare earth elements (REEs, La through Yb) are shown for reference.

up to atomic number 50; beyond that, elements are less abundant. The elemental composition of the solar system is similar to that of the universe, but with the caveat that inner planets (Earth included) are enriched in heavier elements relative to outer planets – note the differences in Figures 1.1 and 1.2.

It is also clear that some elements appear to be anomalously uncommon as compared to their neighbors (e.g. Li, Be, B, Sc), whereas others seem to be present in anomalously high concentrations (e.g. Fe, Ni, Pb). It is also interesting to note the sawtooth pattern produced by alternation of relatively abundant even-numbered elements as compared to neighboring odd-numbered elements (a phenomenon described by the Oddo-Harkins rule). How do these observed trends relate to the processes that formed the elements? The answer lies in basic principles of nuclear fusion.

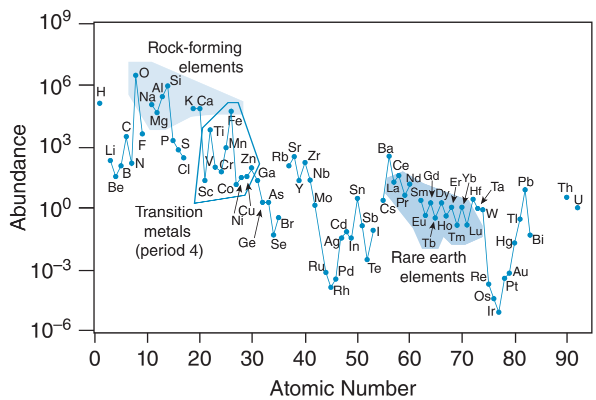

Fig. 1.2 Abundance of the elements in Earth's upper continental crust (molar basis) as a function of atomic number, and normalized to Si = 10^6 on a logarithmic y-axis.

1.2.2 Formation of heavier elements

Elements larger than He were formed by fusion in stars in the first few million to hundreds of millions of years after the Big Bang by a process generally referred to as *stellar nucleosynthesis*. Gravitational forces had produced a contracting, spinning disc-like mass of primordial H and He known as the solar nebula, which contained the energy necessary to form heavier elements by fusion as follows:

$$^{4}_{2}\mathrm{He} + ^{4}_{2}\mathrm{He} = ^{8}_{4}\mathrm{Be} + \gamma \quad (1.2)$$

$$^{4}_{2}\mathrm{He} + ^{8}_{4}\mathrm{Be} = ^{12}_{6}\mathrm{C} + \gamma \quad (1.3)$$

$$^{12}_{6}\mathrm{C} + ^{12}_{6}\mathrm{C} = ^{20}_{10}\mathrm{Ne} + ^{4}_{2}\mathrm{He} \quad (1.4)$$

Focus Box 1.3

Composition of the Universe vs. Earth

The vast majority of the mass in the universe (97–98%) consists of H and He that remain from the first few minutes following the Big Bang. These two elements formed the base fuel for subsequent stellar nucleosynthesis in the cores of stars that resulted in heavier elements. The composition of Earth is skewed toward relatively high abundance of these heavier elements (Table 1.1; Figure 1.2), as much of the lighter H and He were lost to outer space (H was retained to a far greater extent than He because H occurs in water, which is held by gravitational force in a way that gaseous He was not).

Table 1.1 Chemical differentiation of earth with major elements and selected trace elements.

	Granite	Basalt	Ultramafic	Sandstone	Shale	Carbonate
SiO_2	69.4	49.3	42.1	71.3	64.8	8.34
TiO_2	0.48	1.86	0.05	0.70	0.80	0.12
Al_2O_3	15.4	15.3	2.25	10.6	17.0	1.52
Fe_2O_3*	2.66	12.0	13.7	5.03	5.70	1.07
MnO	0.03	0.22	0.20	0.10	0.25	0.07
MgO	0.75	7.39	38.2	2.52	2.83	21.2
CaO	1.96	9.9	2.22	3.03	3.51	66.7
Na_2O	4.08	2.47	0.66	1.56	1.13	0.21
K_2O	4.48	0.98	0.02	4.61	3.97	0.55
P_2O_5	0.14	0.25	0.04	0.16	0.15	0.07
SUM	*99.4*	*99.7*	*99.4*	*99.7*	*100.1*	*99.8*
As	0.25	2.2	0.8[a]	1.0	28	1.6
Ba	1880	315	0.7	595	636	99
Cr	10*	185	1800	20	125	10
Co	4.6	47	175	2.3	20*	3.6
Cu	11	94	15	2.5	45*	1.3
Ni	10*	150	2000	10.1	58	3.3
Pb	30	7	0.5	8.3	20*	2.8
Sr	275	465	1	20	300	610
Th	13*	3.5	0.005	4.4	12.3	0.54
U	3*	0.75	0.002	1.3	2.7	1.6
Zn	86	120	40	50	95*	13

Major elements (SiO_2 through P_2O_5) are presented in units of wt % oxides and the trace elements are presented in concentrations of parts per million (ppm, or mg/kg). Data sources are as follows: granite is the United States Geological Survey granite standard "G-2"; basalt and ultramafic data are averages from Turekian and Wedepohl (1961) and Vinogradov (1962); sandstone and carbonate rock data are unpublished analyses of early Paleozoic sedimentary rocks from northwestern Vermont performed by the author; and shale is the North American Shale Composite (Gromet et al., 1984). Sr and the other trace element values with asterisks are averages from Turekian and Wedepohl (1961) and Vinogradov (1962).

[a] Indicates highly variable, from <1 ppm to >500 ppm, depending on metamorphic fluids. Additional resources include the text *The Continental Crust: its Composition and Evolution* by Taylor and McLennan (1985) and the chapter by Rudnick and Gao (2003) in *Treatise on Geochemistry*.

This process skipped over odd-numbered Li and B (atomic numbers 3 and 5) and the $^{8}_{4}$Be that formed was very unstable and was either rapidly transformed to ^{12}C before it decayed, (Eq. (1.3)) or was destroyed by radioactive decay.

Fusion was able to form elements up to iron ($^{56}_{26}$Fe), but beyond that no heat is released during fusion – that is, the process is no longer exothermic when fusing nuclei heavier than Fe. In fact, the iron nucleus is so stable that fusion reactions involving iron actually consume energy (i.e. an endothermic process), so without the heat needed to fuel fusion reactions, another process had to take over to form the heavier elements. This process is known as neutron capture and can be represented like this:

$$^{56}_{26}\text{Fe} + ^{1}_{0}\text{n} = ^{57}_{26}\text{Fe} \qquad (1.5)$$

$$^{57}_{26}\text{Fe} + ^{1}_{0}\text{n} = ^{58}_{26}\text{Fe} \qquad (1.6)$$

$$^{58}_{26}\text{Fe} + ^{1}_{0}\text{n} = ^{59}_{26}\text{Fe} \qquad (1.7)$$

The Fe^{59} atom is unstable and undergoes spontaneous radioactive decay to cobalt by beta emission as follows:

$$^{59}_{26}\text{Fe} = ^{59}_{27}\text{Co} + \beta^{-} \qquad (1.8)$$

In this case, the negatively charged beta particle (sometimes written as $^{0}_{-1}e$ or e^{-}) can be thought of as the product of the transformation of a neutron ($^{1}_{0}$n) to a proton ($^{1}_{1}$p), which requires $^{0}_{-1}e$ on the product side to balance the reaction. Neutron capture combined with radioactive decay then formed progressively heavier elements up to the heaviest naturally occurring element, uranium. Some elements such as ^{56}Ni and ^{56}Co are unstable and undergo radioactive decay to form stable ^{56}Fe, helping to explain the relative abundance of Fe as compared to elements with similar atomic number.

Returning to fusion, it is clear that progressive fusion reactions involving atoms with even numbers of protons will lead to the sawtooth pattern in Figure 1.1, but there is also another contributing factor to this pattern, and that is the *Oddo-Harkins rule*: atoms with an even number of protons in their nuclei are more stable than their odd-numbered counterparts. This is because, during nucleosynthesis, nuclei with an unpaired proton were more likely to capture an additional proton, producing a more stable proton arrangement, and this favors nuclei with even numbers of protons. For additional information on nucleosynthesis and the origin of the elements, the reader is referred to the accessible and more detailed presentation in Gunter Faure's text *Principles and Applications of Geochemistry*.

1.2.3 Formation of planets and compositional differentiation

As the universe continued to cool, galaxies and solar systems began to form. The solar nebula that was to form our solar system cooled and began to solidify into small masses known as chondrites and eventually larger masses known as planetesimals (on the order of 10s of km in diameter) approximately 5 billion years ago (the Earth is ~4.6 billion years old). Those closest to the early sun became enriched in heavier elements (especially Si, Al, Mg, Fe, Ca, Na, K), in part because centrifugal forces effectively flung lighter elements (especially H and He) preferentially to the farther reaches of the solar system (other important influences include temperature, pressure, redox conditions, and nebular density, but these factors are not covered here). The result is that the inner planets are terrestrial and rocky (Mercury through Mars) and enriched in heavier elements, whereas the outer planets are gaseous (Jupiter and beyond) and enriched in lighter elements (think of the possibility of methane oceans or methane ice on Saturn's moon Titan).

Planets ultimately formed when gravitational forces caused accretion of planetesimals. The accretion of

Focus Box 1.4

How Neutron Capture Works

Neutron capture (Eqs. (1.5)–(1.7)) takes place via two main mechanisms. The *r-process* ("r" is for rapid) takes place in core-collapse supernovae, where high neutron flux and extremely high temperatures (e.g. $>10^9$ K) facilitate nucleosynthesis involving a rapid series of neutron capture reactions starting (typically) with ^{56}Fe – the r-process explains the origin of ~50% of atoms heavier than Fe. The other main means by which heavy elements can be produced is known as the *s-process* ("s" is for secondary), in which nucleosynthesis occurs by means of slow neutron capture. The difference is that s-process neutron-capture nucleosynthesis occurs in asymptotic giant branch (AGB) stars, which have lower temperatures (e.g. 10^3–10^4 K) than supernovae, and thus the s-process requires preexisting (hence the "secondary" nature) heavy isotopes that can function as seed nuclei.

Focus Box 1.5

Rock Geochemistry and Soil Composition

Compositional differentiation of the earth – and specifically with reference to different rock types – often exerts a strong control on the composition of soils. A good example is the weathering of ultramafic rocks (e.g. serpentine, peridotite) derived from the mantle – these ultramafic soils tend to be depleted in plant nutrients such as Ca and K, and enriched in the trace metals Ni and Cr (and in some places, arsenic [As]). Examine Table 1.1 to get an idea of the impact that different rock types can impose on composition of associated soils and waters.

what was to become Earth produced heat that left the proto-planet in a molten or semi-molten state and allowed relatively dense Fe and nickel (Ni) to sink to the *core of the Earth*, whereas relatively light silicon (Si), aluminum (Al), magnesium (Mg), calcium (Ca), sodium (Na), and potassium (K) floated to the top to form *Earth's crust*, leaving the Fe–Mg–Ni–Cr–Si *mantle* in between core and crust. While this is a broad generalization, the result is a differentiated Earth (Table 1.1), one where average continental crust (~ between 25 and 60 km thick) has a felsic composition much like that of granite, whereas oceanic crust (~ between 5 and 10 km thick) is, on average, compositionally mafic (or basic) and comprised mainly of basalt, rock that is less silica-rich (less SiO_2-rich) and relatively enriched in Fe, Mg, and Ca relative to continental crust. The mantle is comprised of rock types like peridotite and dunite and has an ultramafic (or ultrabasic) composition.

The primordial atmosphere of earth was comprised of CO_2, CH_4, H_2O, and N gases derived from volcanic eruptions. Oxygen in its form as O_2 gas is a relatively recent addition to earth's atmosphere, having begun to accumulate slowly and in a stepwise manner in the atmosphere after the appearance of photosynthetic algae 3 billion years ago. More on this topic is presented in Chapter 7.

1.3 ATOMS, ISOTOPES, AND VALENCE ELECTRONS

1.3.1 Atoms: protons, neutrons, electrons, isotopes

A pair of schematic sketches of the carbon atom, consisting of a central positively charged nucleus surrounded by a negatively charged "cloud" of electrons, is presented in Figure 1.3. All atoms consist of a nucleus that contains positively charged *protons* and neutral *neutrons*, both subatomic particles with a mass of 1 atomic mass unit (1 amu, or 1 Dalton [Da]).

The actual mass of a proton is 1.6726×10^{-24} g, so it is more convenient to say that the mass of a proton is 1 amu or 1 Da. The +1 charge on a proton = 1.602×10^{-19} coulomb. The number of protons in the nucleus is what distinguishes atoms of one element from another – hydrogen has 1 proton, helium has 2, carbon has 6, uranium has 92, and so on. If there is a nucleus with some other number of protons than 92, it is not uranium. The number of protons is commonly referred to as the *atomic number* (Z).

The mass of a neutron is effectively the same as the mass of a proton (1 amu; 1.6749×10^{-24} g), and sum of protons

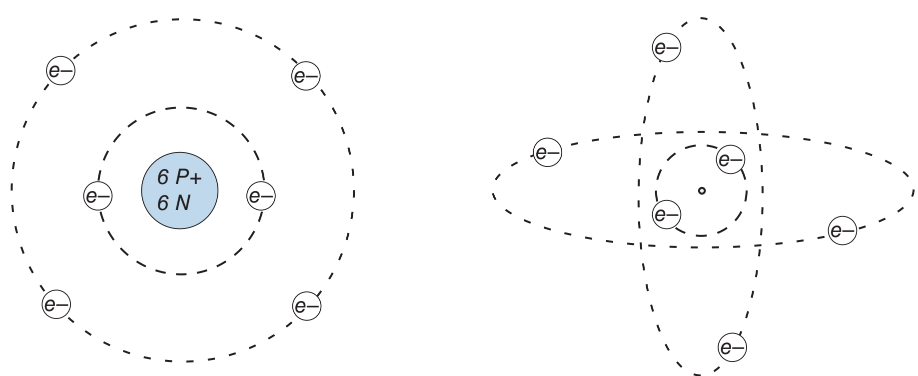

Fig. 1.3 Schematic sketches of Bohr models of a carbon atom (^{12}C) showing, on the left, 6 protons and 6 neutrons in the nucleus with 6 electrons in 2 separate orbitals, and on the right, an atom that attempts to show the actual size of the nucleus compared to the electron cloud, yet even here the nucleus is ~100 times larger than an actual nucleus. The example on the right also introduces the idea of separate orbitals in the outer electron "shell."

and neutrons is the *atomic mass* or *mass number* or *atomic weight* – all are essentially synonymous terms. Virtually all of the mass of an atom is contained in its nucleus. The carbon atom in Figure 1.3 contains a nucleus with 6 protons and 6 neutrons, a configuration represented in this text and in many other places as ${}^{12}_{6}C$. So, while the number of neutrons is not explicitly given in this notation, it is implied, and in the case of the most common form of uranium, ${}^{238}_{92}U$, there must be 146 neutrons in the nucleus along with 92 protons to produce the atomic mass of 238.

The carbon atom in Figure 1.3 contains 6 protons and likely also contains 6 neutrons, but it could contain 7 or 8 neutrons. Differences in the number of neutrons (6, 7, or 8) give rise to the three *isotopes* of carbon. Carbon-12, or ${}^{12}C$, is the most abundant isotope of carbon and it contains 6 neutrons; ${}^{13}C$ contains 7 neutrons and it is much rarer than ${}^{12}C$ (Chapter 10). ${}^{12}C$ and ${}^{13}C$ are both stable isotopes of carbon and the ratios of these two isotopes in plants, rocks, waters, and sediments have proven very useful in environmental analysis. Carbon also has a *radioactive isotope*, ${}^{14}C$, which is produced in the atmosphere in the presence of cosmic rays. Atoms of ${}^{14}C$ are unstable and undergo radioactive decay to nitrogen. This topic and many others in the field of isotope geochemistry are covered in Chapters 10 and 11.

1.3.2 Electrons and bonding

Electrons balance the positive charge of the protons. Electrons are located in specified positions, or energy levels, outside of the nucleus, and the charge on an electron is exactly opposite that of a proton, i.e. −1, or -1.602×10^{-19} coulomb, and neutrally charged atoms contain equal numbers of protons and electrons. Furthermore, while the "electron cloud" surrounding the nucleus is of a virtually negligible mass, it occupies a volume that is orders of magnitude larger than the volume of the nucleus (atoms are mostly open space). (This is shown schematically on the right side of Figure 1.3.)

For the purpose of this text and virtually all environmental geochemistry, the main concern to investigators is the outermost shell of electrons (the *valence shell*), because that is the part of the atom most intimately involved in bonding and ionization. One convenient way to depict valence electrons is with *Lewis electron dot diagrams* (Figure 1.4). Sodium, with one valence electron, and oxygen, with six, can be depicted as shown in Figure 1.4.

Sodium satisfies the octet rule by losing an electron, becoming Na^+. The neutral oxygen atom with six valence electrons can most easily satisfy the octet rule by gaining two electrons, producing O^{2-}, the most common form of oxygen in nature.

The *Aufbau principle* describes how electron orbitals are populated in a systematic manner. In brief, electrons occupy orbitals of fixed energy levels and tend to occupy the lowest energy levels possible to create a stable atom. Orbitals are filled in a relatively predictable, sequential manner, starting with the lowest quantum number ($n = 1$), for which there is only one orbital (the *s*-orbital) which can be occupied by two electrons (of opposite spin).

For a neutral hydrogen atom with only one electron, the symbol is $1s^1$. For neutral He with 2 electrons, the notation is $1s^2$. Quantum number 2 ($n = 2$) contains

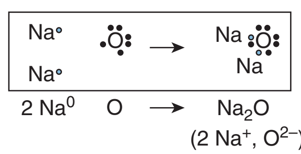

Fig. 1.4 Lewis electron dot diagrams showing valence electrons of sodium and oxygen in their ground states (left) and in the compound Na_2O (right), where each sodium has lost an electron to oxygen, resulting in two Na^+ and one O^{2-}. The oxygen atom on the left is an idealized representation because in reality it would likely be an O_2 molecule.

Focus Box 1.6

Octet Rule Considerations

Neutral atoms with atomic number (Z) ≤ 20 contain somewhere between 1 and 7 electrons in their valence (outermost) shell; the noble gases Ne and Ar contain 8 valence shell electrons. The most stable valence shell electron configuration for elements with Z ≤ 20 is one that consists of 8 electrons, so all atoms with Z ≤ 20 seek to produce ions or form bonds that result in eight valence electrons. They do this either by losing, gaining, or sharing electrons. For elements with Z > 20, the presence of d and f orbitals makes the octet rule inapplicable; nonetheless, heavier elements lose electrons in predictable manners to form more stable configurations, and the forms of these ions are commonly known (e.g. Fe^{2+} and Fe^{3+}; Ni^{2+}; U^{4+}, and U^{6+}) which enables prediction of their behaviors in environmental systems.

Focus Box 1.7

Aufbau Examples

Two useful examples of larger atoms in the Aufbau scheme are calcium and iron. The notation for calcium is: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$. Note that the second and third quantum levels contain eight electrons, but that the fourth contains only two. What must calcium do to satisfy the octet rule when forming an ion? It loses two electrons, taking on an electron configuration like that of argon ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$) and becoming Ca^{2+}. (Note: the notation for Ca is often abbreviated as $[Ar]4s^2$.) The notation for iron is: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$ (26 electrons balance the 26 protons to produce a neutral Fe atom). At this point the octet rule does not exactly predict common oxidation states – iron tends to occur as Fe^{2+} or Fe^{3+} depending on redox conditions (more to come on redox later in this chapter).

both *s*- and *p*- orbitals, where the *s*-orbital again can be occupied by one electron pair and the *p*-orbital can host up to 3 electron pairs. For neutral lithium with 3 electrons, the notation is $1s^2\ 2s^1$. For neutral oxygen, the notation is $1s^2\ 2s^2\ 2p^4$ (to satisfy the octet rule, oxygen gains two electrons, producing the O^{2-} anion with an electron configuration like that of neon: $1s^2\ 2s^2\ 2p^6$). The third quantum level ($n = 3$) contains *s*-, *p*-, and *d*-orbitals, where the *s*- and *p*-orbitals can contain 1 and 3 electron pairs, respectively, and the *d*-orbital can host 5 electron pairs (10 e^-s). However, the 3*d* orbital exists at a higher energy level than the 4*s* orbital, so the 4*s* orbital is filled before the 3*d*. The sequence in which these orbitals are filled is as follows:

$$1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p \rightarrow 5s \rightarrow 4d \rightarrow 5p \rightarrow 6s \rightarrow 4f \rightarrow 5d \rightarrow 6p \rightarrow 7s \rightarrow 6d$$

1.4 MEASURING CONCENTRATIONS

Concentrations of elements or compounds are measured in a few common ways. Only in rare cases do scientists directly measure individual atoms/compounds, and this is because even microscopic crystals of minerals at the micrometer scale such as hydroxides and silicate clays typically contain millions or billions of atoms.

1.4.1 Mass-based concentrations

One common means of measuring concentrations is by units such as milligrams per kilogram (mg kg^{-1}) for solids and milligrams per liter (mg l^{-1}) for liquids, or sometimes in units of micrograms (μg kg^{-1} or μg l^{-1}) or nanograms (ng kg^{-1} or ng l^{-1}) for trace elements. Note that mg l^{-1} = μg ml^{-1}. Weight percent is a common mass-based approach for expressing element concentration in cases where elements are in high concentrations (e.g. Table 1.1), a good example being Si, which comprises approximately 28% by weight (or mass) of the continental crust, but as wt % oxide, approximately 59% of the crust – this conversion is presented here.

Weight percent oxide is a common means of expressing major (abundant) elements in soils and rocks. Note in Table 1.1 that Si, Al, Fe, and the other major elements are presented in units of SiO_2, Al_2O_3, Fe_2O_3, and so on. This is done partly by convention (or habit) and also because the major elements tend to occur in silicate minerals bonded to oxygen. The conversion factors for wt % element to wt % oxide for the common oxides are presented here in Table 1.2 (where C.F. = conversion factor).

In the case of converting Ca to CaO, the conversion is determined as the molar mass of CaO divided by the molar mass of Ca, i.e. $56.08 \div 40.08 = 1.399$.

Focus Box 1.8

A Few Useful Facts About Mass-Based Units of Concentration

For solids:
mg kg^{-1} is also known as parts per million (ppm), where mg is a milligram (10^{-3} g)
μg kg^{-1} is also known as parts per billion (ppb), where μg is a microgram (10^{-6} g)
ng kg^{-1} is also known as parts per trillion (ppt), where ng is a nanogram (10^{-9} g)

For liquids:
mg l^{-1} is also known as parts per million (ppm)
μg l^{-1} is also known as parts per billion (ppb)
ng l^{-1} is also known as parts per trillion (ppt)

Focus Box 1.9

Molar vs. Mass-Based Units

Mass-based measurements like μg l^{-1} or wt % are not always the best way to express concentrations. Consider for example groundwater with 98.7 μg l^{-1} each of nickel (^{59}Ni) and uranium (^{238}U); i.e. both elements are present in equal concentrations of 98.7 ppb. We could visualize this by evaporating the liter of water, which would leave 98.7 μg each of Ni and U. Consider this though: given that U atoms (238 g mol^{-1}) are ~4 times heavier than Ni (59 g mol^{-1}), there must be more Ni atoms; in fact, there are approximately four times as many Ni atoms as there are U atoms.

Table 1.2 Conversion factors for wt % element to wt % oxide.

Element	C.F.	Oxide
Al	1.889	Al_2O_3
Ca	1.399	CaO
Fe	1.286	FeO
Fe	1.430	Fe_2O_3
K	1.205	K_2O
Mg	1.658	MgO
Mn	1.291	MnO
Na	1.348	Na_2O
P	2.291	P_2O_5
Si	2.139	SiO_2
Ti	1.668	TiO_2

In the case of Al_2O_3, the conversion factor is determined as the molar mass of Al_2O_3 divided by the mass of the equivalent amount of Al in the oxide, i.e. $Al_2O_3 \div (2 \times Al) = 101.957 \div (2 \times 26.98) = 1.889$. For Na to Na_2O, the conversion is the molar mass of Na_2O divided by the molar mass of $2\times Na = 61.98 \div (2 \times 22.99) = 1.348$.

For elements that can occur in more than one oxidation state (e.g. Fe^{2+}, Fe^{3+}), values may be presented as either one of the oxidation states (i.e. either as FeO or Fe_2O_3), or as a combination of the two if the relative abundances of Fe^{2+} and Fe^{3+} are known. In many cases where iron oxidation state is not known, all iron is presented in terms of Fe_2O_3.

1.4.2 Molar concentrations

Quantifying concentrations on a molar basis has its roots in the work of Italian scientist Amadeo Avogadro, who in 1811 realized that equal volumes of gases at identical pressures and temperatures contain equal numbers of atoms (or molecules in the case of gases like N_2 and O_2), even though their atomic masses differ. The term *mole* (abbreviated mol) describes the number of atoms of a given element required to form a mass equal to the atomic mass of the substance, in grams. For C, this mass is 12.011 g. For U, this mass is 238.03 g, and so on. For all elements, the number of atoms required to form the atomic mass in grams is 6.0221×10^{23} atoms, a value known as *Avogadro's number*. What this means is that 238.03 g of uranium (1 mol of U) contains 6.0221×10^{23} atoms; similarly, 4.002 g of helium (1 mol of He) contains 6.0221×10^{23} atoms.

Focus Box 1.10

Converting Mass-Based to Molar Concentrations

The mole is a very useful concept in chemistry, especially considering that chemical equations are expressed in terms of moles of reactants and products. In order to express Ni and U concentrations in terms of moles per liter (mol l^{-1}), or for trace elements like these, μmol l^{-1}, the mass concentration must be multiplied by the inverse of the molar mass (and a conversion for g to μg) as follows:

For Ni: $98.7\ \mu g\ l^{-1} \times 1\ mol/58.693\ g \times 1\ g/10^6\ \mu g = 1.68 \times 10^{-6}\ mol\ l^{-1}$

For U: $98.7\ \mu g\ l^{-1} \times 1\ mol/238.03\ g \times 1\ g/10^6\ \mu g = 0.415 \times 10^{-6}\ mol\ l^{-1}$

It is often helpful to express units in easy to communicate terms, so in this case mol l^{-1} would probably be converted to micromoles per liter (μmol l^{-1}), by multiplying mol l^{-1} by 10^6 μmol mol^{-1}:

$1.68 \times 10^{-6}\ mol\ l^{-1} \times 10^6\ \mu mol\ mol^{-1} = 1.68\ \mu mol\ l^{-1}$ of Ni in the groundwater

$0.415 \times 10^{-6}\ mol\ l^{-1} \times 10^6\ \mu mol\ mol^{-1} = 0.415\ \mu mol\ l^{-1}$ of U in the groundwater

In a solid (e.g. sediment or rock) with 1 mol kg^{-1} each of Fe (55.85 g mol^{-1}) and Al (26.98 g mol^{-1}): (i) there is an equal number of atoms of Fe and Al in the soil; and (ii) Fe comprises a greater mass of the soil than Al (whether expressed as wt %, g kg^{-1}, or mg kg^{-1}). Given that mass units are a common way of expressing concentration, it may be necessary to convert from molar units to mass units. A few algebraic calculations allow conversion from mol kg^{-1} to 3 common units, g kg^{-1}, mg kg^{-1}, and wt% ($0.1 \times$ g kg^{-1}):

Given that 1 mol of Fe = 55.85 g:

$$55.85\ \mathrm{g\ mol^{-1}} \times 1\ \mathrm{mol\ kg^{-1}} = 55.85\ \mathrm{g\ kg^{-1}\ Fe}$$

. . . or

$$55.85\ \mathrm{g\ kg^{-1}} \times 1000\ \mathrm{mg\ g^{-1}} = 55\,850\ \mathrm{mg\ kg^{-1}\ Fe}$$

. . . or

$$55.85\ \mathrm{g\ kg^{-1}} \times 0.1 = 5.855\%\ \mathrm{Fe\ (by\ weight)}$$

$$1\ \mathrm{mol\ of\ Al} = 26.98\ \mathrm{g};\ 26.98\ \mathrm{g\ mol^{-1}} \times 1\ \mathrm{mol\ kg^{-1}} = 26.98\ \mathrm{g\ kg^{-1}\ Al}$$

. . . or

$$26.98\ \mathrm{g\ kg^{-1}} \times 1000\ \mathrm{mg\ g^{-1}} = 26\,980\ \mathrm{mg\ kg^{-1}\ Al}$$

. . . or

$$26.98\ \mathrm{g\ kg^{-1}} \times 0.1 = 2.698\%\ \mathrm{Al\ (by\ weight)}$$

1.4.3 Concentrations of gases

Atmospheric gas concentrations are typically expressed as the proportion of the total volume accounted for by a given gas. For example, the current atmospheric concentration of CO_2 is ~ 410 ppmv, indicating that 410 out of every one million molecules of gas in earth's atmosphere is CO_2. At the onset of the industrial revolution atmospheric CO_2 was 280 ppmv. Less-abundant gases are often expressed in terms of pptv or ppbv (parts per billion or trillion, volumetrically), and the major components of the atmosphere like the fixed gases N_2, O_2, and Ar, are expressed in terms of percent (by vol): $N_2 = 78.1\%$, $O_2 = 20.9\%$, and Ar = 0.9% (the amounts vary depending on the amount of H_2O vapor in the air, which can range from 0% to 4% by volume). Expressed in this way, CO_2 comprises approximately 0.041% percent of the atmosphere (vol %), but clearly units of ppmv are more useful for a gas like CO_2. Gases also dissolve in liquids, and units of concentration in these cases are commonly mg l^{-1} or mmol l^{-1}.

1.4.4 Notes on precision and accuracy, significant figures, and scientific notation

A few important considerations related to data analysis and presentation of results are embodied in the concepts of precision and accuracy. Simply stated, *accuracy* describes how closely a measured value agrees with the actual value. The accuracy of chemical analyses can be tested by analyzing standards of known concentration. Consider a certified standard solution that contains 250 mg l^{-1}

Focus Box 1.11

Expressing Uncertainty or Error

One way to express scatter or uncertainty is to determine the standard deviation of the data (many scientists use spreadsheets for this, for which there are many tutorials on the internet). The formula for standard deviation and details on its appropriate use can be found in a statistics textbook, but using the Microsoft Excel ® standard deviation formula produces σ values as follows:

For the values 237, 271, 244, 262, and 240 mg l^{-1}, $\sigma = 14.9$

For the values 277, 281, 274, 278, and 275 mg l^{-1}, $\sigma = 2.7$

For the first set, we could report results as: 251 ± 14.9 mg l^{-1} (1 sd)

For the second set, we could report the results as: 277 ± 2.7 mg l^{-1} (1 sd)

If these data are for a 250.0 ppm standard, which do you consider better, analyses with greater accuracy but less precision (251 ± 14.9 mg l^{-1}), or greater precision but less accuracy (277 ± 2.74 mg l^{-1})? Precise values are easier to correct because there is less uncertainty than if you have to deal with accurate mean values plagued by low precision. This emphasizes one of the reasons it is important to run standards when making analytical measurements. Of course, the ideal situation is to use a well-calibrated instrument for which accuracy and precision are both high, but regardless, it is imperative that researchers seek to quantify both parameters when making measurements.

Focus Box 1.12

Thoughts on Significant Figures

When considering significant figures, it is important to understand the significance of zeros. Consider the following values: 7200, 700 043, 0.0436, 0.043600. How many significant figures are reported for each, and why?

1. 7200 is assumed to have 2 significant figures because any zero at the end of a number and before a decimal point is assumed to not be significant. How many significant figures does 847 000 possess? Three. 7200.0 contains 5 significant figures.
2. 700 043 has 6 sig figs. Any zeros within a number are significant.
3. 0.0436 has 3 sig figs because any zeros after a decimal point and before the first non-zero digit are not significant.
4. 0.043600 has 5 significant figures because zeros that follow a non-zero digit after a decimal point are considered significant. (as in 7200.0 example above).

Some of these examples serve to illustrate why scientists tend to express values in terms of ***scientific notation***. Using scientific notation, the values above become:

7.2×10^3 (2 sig figs)
7.2000×10^3 (if we needed to report 7200 to 5 sig figs, this is how it would look)
7.00043×10^5 (6 sig figs)
4.36×10^{-2} (3 sig figs)
4.3600×10^{-2} (5 sig figs)

of aluminum (Al), and five analyses of this standard on your spectrometer produces results of 237, 271, 244, 262, and 240 mg/l. The mean of those five values is $251\ \text{mg l}^{-1}$ – the average value is very close to the certified value of $250\ \text{mg l}^{-1}$. One way to express the accuracy of this test is as a percent difference from the certified value:

$$[(251\ \text{mg l}^{-1} - 250\ \text{mg l}^{-1}) \div 250\ \text{mg l}^{-1}] \times 100 = 0.4\%$$

However, the five results are somewhat lacking in *precision*, which is basically a measure of the reproducibility of results – how closely do measured results agree with each other?

It is conceivable to produce results with a high degree of precision that are lacking in accuracy. For example, after recalibrating the spectrometer and re-analyzing the Al standard, values now are 277, 281, 274, 278, and $275\ \text{mg l}^{-1}$. The mean value of $277\ \text{mg l}^{-1}$ is farther from the certified value of $250\ \text{mg l}^{-1}$ (the difference from the certified value is 10.8%), but the results are definitely more precise.

In addition to quantifying uncertainty, it is very important to present numerical results in a manner that relates to the sensitivity of the measurement, or the degree of confidence associated with that measurement, while also trying to avoid propagation of error. Every measurement has some limited number of *significant digits* (or *significant figures*). Measurements of pH made using litmus paper can only be reported to 1 significant figure (e.g. pH = 6) whereas measurements made with well-calibrated probes may be reported to 3 significant figures (e.g. pH = 5.87).

As a rule, calculations should be carried out using all figures with each of their representative significant figures, and then the final result should be rounded at the end of the calculation. Using an example where the average concentration of uranium in groundwater in an aquifer is $14.3\ \mu\text{g l}^{-1}$, the aquifer volume is $1.241 \times 10^8\ \text{m}^3$, and average porosity (and thus % water in the saturated zone) is 1.8%, resulting mass of U in the aquifer is:

$$14.3\ \mu\text{g l}^{-1} \times 1.241 \times 10^8\ \text{m}^3 \times 1000\ \text{l m}^{-3} \times 0.018 = 3.2 \times 10^{11}\ \mu\text{g U}$$

The final result is limited by the two significant figures in 1.8% (note that conversions involving liters to cubic meters, cm^3 to ml, etc. do not limit sig figs).

As a closing thought on this topic, the precision of the road sign in southwestern Ecuador shown in Figure 1.5 is notable. Being literal about significant figures, the distance to Engunga is precisely indicated as being between 14.995 and 15.005 km, a level of precision down to ≤ 10 m (note: it is a very small town, so the precision may be justified).

Fig. 1.5 Road sign in coastal Ecuador showing high level of precision.

1.5 PERIODIC TABLE

The Periodic Table of the Elements (*inside front book cover*) is a very useful tool for researchers and students of chemistry, geochemistry, and biochemistry. First developed by the Russian chemist Dmitri Mendeleev in 1869 and refined ever since, it lists elements in order of atomic number (from left to right in each row, and also from top to bottom in each column) and by similarities in chemical properties. For example, row 3 of the periodic table begins with sodium (atomic number Z = 11) and progresses to the right with increasing Z all the way up to argon (Z = 18).

1.5.1 Predicting behavior of elements using the periodic table

Columns (or groups) generally contain elements with similar valence electron configurations, that is, the outermost shell of electrons tends to be arranged in a similar manner for elements of a given group. Good examples are group 1, the alkali metals, all of which lose one electron when they form chemical bonds, resulting in a series of 1+ charged ions including Na^+ and K^+; group 2, the alkaline earth metals that form divalent cations (e.g. Mg^{2+}, Ca^{2+}, Sr^{2+}); group 3 ions include B^{3+} and Al^{3+}. In group 4, silicon occurs as Si^{4+} but carbon is much more complex, ranging from C^{4+} to C^{4-} and various oxidation states in between (Chapter 5, Section 5.2.1). On the right side of the periodic table, the group 8 noble gases include elements like argon and neon with complete valence shells (as a result, they do not form chemical bonds in nature). The group 7 halogens tend to gain one electron when forming chemical bonds, resulting in halide anions like F^- and Cl^-. Oxygen in group 6 is O^{2-} in nearly all compounds, and in reducing environments sulfur occurs as S^{2-}.

It may not come as a surprise that alkali metals tend to form bonds with halides, such as:

$$Na^+ + Cl^- \rightarrow NaCl \tag{1.9}$$

The point to understand here is that the periodic table presents information in a systematic way that can help to predict the behavior of elements in environmental systems. Like Na^+, K^+ can also form bonds with chloride (Cl^-) to form a different salt, KCl (a substitute for NaCl in reduced-sodium diets). In fact, K^+ and Na^+ substitute for one another in many minerals. The periodic table also implies that arsenic (As) might substitute for phosphorus (P) in molecules, which it does.

1.5.2 The earth scientist's periodic table

In 2003, the environmental geochemist Bruce Railsback from the University of Georgia developed an innovative new periodic table for geologists known as *An Earth Scientist's Periodic Table of the Elements and Their Ions*,

Focus Box 1.13

Atomic Mass of Sulfur

The atomic mass for each element represents a weighted average of the mass of the isotopes of that element – the following is a mass-balance calculation that takes into account the weighted average of ^{32}S and the three naturally occurring heavier isotopes of S (data from Faure 1986):

$^{32}S = 95.02\%$	$^{33}S = 0.75\%$	$^{34}S = 4.21\%$	$^{36}S = 0.02\%$

$$\begin{aligned}
^{32}S&: 0.9502 \times 31.97\ g\ mol^{-1} = 30.377894\ g\ mol^{-1}\\
^{33}S&: 0.0075 \times 32.97\ g\ mol^{-1} = 0.247275\ g\ mol^{-1}\\
^{34}S&: 0.0421 \times 33.97\ g\ mol^{-1} = 1.430137\ g\ mol^{-1}\\
^{36}S&: 0.0002 \times 35.97\ g\ mol^{-1} = \underline{0.007194\ g\ mol^{-1}}\\
&\qquad\qquad \text{Sum} = 32.062500\ g\ mol^{-1}
\end{aligned}$$

Atomic masses for elements are expressed in terms gram molecular weights (i.e. the gram molecular weight, or mass of 1 mol of sulfur, is 32.06 g). Note that here the atomic mass is represented with 4 significant figures. The reason that each of the isotopes is not an integer value (e.g. ^{32}S is stated as 31.97 rather than 32.0 g mol^{-1}) is that all atomic masses are normalized to the mass of ^{12}C.

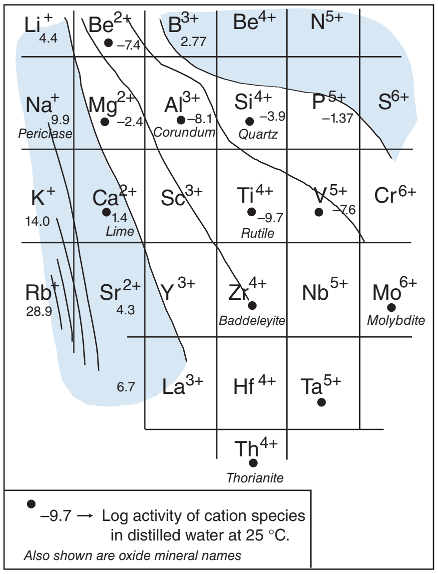

Fig. 1.6 Solubilities of ions as a function of ionic charge, from Inset 4 of *An Earth Scientist's Periodic Table of the Elements and Their Ions* (Railsback, 2003). Oxides of the elements are used as reference (e.g. lime, periclase, etc.). Note that low-charge base cations/alkali metals and cations of the alkaline earth metals are relatively soluble, as are high-charge cations such as S^{6+} and N^{5+}, which form polyatomic anions (SO_4^{2-}, NO_3^-). Cations with +3 and + 4 charges (e.g. Al^{3+}, Ti^{4+}, Zr^{4+}) are insoluble in most surficial environments, with activities in H_2O at 25 °C of $\sim 10^{-8}$ to 10^{-10}.

one where elements are organized according to their occurrences in geological environments (http://www.gly.uga.edu/railsback/PT.html). This new formulation is designed to predict how elements and ions behave in the environment. Unlike the conventional periodic table originally envisioned by Mendeleev, the earth scientist's periodic table organizes elements by charge, so it shows many elements multiple times because many elements have numerous oxidation states. It also contains plentiful information on abundance of different elements in soils, seawater, mantle vs. crust, ionic radii in crystals, and much more. For example, Figure 1.6 shows the relative solubilities of oxides of various ions, and from this inset it is apparent that Al and Ti form insoluble oxides (corundum, Al_2O_3; rutile, TiO_2) but that Na, K, N, and S do not (they are more likely to occur as soluble ions such as Na^+, K^+, NO_3^-, and SO_4^{2-}).

The earth scientist's periodic table also shows the numerous species of nitrogen that exist in natural systems (e.g. oxidation states and common molecules of N), predicted behaviors, attributes and affinities of the abundant and trace cations in natural systems, and more (Railsback 2003).

1.6 IONS, MOLECULES, VALENCE, BONDING, CHEMICAL REACTIONS

It is relatively rare to find elements in their native, neutral state in nature. Some elements do occur in neutral states, including the diatomic gases hydrogen (H_2), oxygen (O_2), and nitrogen (N_2), solids like gold (Au), graphite, and diamond (both forms of C), and the noble gases (He, Ne, Ar . . .). Most elements, however, occur as ions, molecules, or compounds in liquids (petroleum, alcohols, H_2O, and the dissolved species it contains), solids (minerals, proteins, humus), and gases (CO_2, CH_4, NO_2). *Ions* are charged atoms, atoms that have either gained or lost one or more electrons from their neutral state. Examples of ions include the cation Na^+ and the anion S^{2-}. Most of the elements form cations, because metals generally lose electrons to form cations, and most of the elements are metals. A few common metal cations are Mg^{2+}, Al^{3+}, $Cr^{3+,6+}$, $Fe^{2+,3+}$ – note that some elements have more than one oxidation state. Generally only those elements in the upper right of the periodic table form anions (e.g. O^{2-}, N^{3-}, F^-, etc). *Oxidation state* is a term for the charge on an ion: "the oxidation state of iron in swamps is generally 2+ (divalent), whereas in streams, iron tends to occur in the 3+ (trivalent) oxidation state."

Molecules form when two or more atoms are joined by a chemical bond, and *compounds* are a specific type of molecule formed when two or more atoms of *different* elements are joined by chemical bonds. The gases H_2, O_2, and N_2 occur as molecules but they are not compounds (they are diatomic gases). Examples of compounds include NaCl, H_2O, and C_8H_{18} (octane). Most substances in nature, other than some gases and a few metals, are compounds.

There are two main types of *chemical bonds* responsible for forming molecules and compounds, ionic bonds and covalent bonds. These two bond types represent polar ends of the bonding spectrum, but it is useful to consider each type separately, and then examine intermediate cases. We will also examine metallic bonds and van de Waals bonds, but first will begin with ionic bonds.

1.6.1 Ionic bonding

Ionic bonds occur between atoms of elements with very different valence electron configurations. Coulomb forces describe interactions between charged atoms or molecules (i.e. ions), and when the charges are opposite (i.e. involving cations and anions), the result is attraction (conversely,

Focus Box 1.14

Oxidation State According to IUPAC

IUPAC is the International Union of Pure and Applied Chemistry and is the authority on questions of nomenclature in chemistry. IUPAC nomenclature (Karen et al. 2016) indicates that "the oxidation state of an atom is the charge of this atom after ionic approximation of its heteronuclear bonds," and that "oxidation state" and "oxidation number" are effectively synonymous terms. In terms applicable to geochemistry, oxidation state is the charge on an atom in a solution (e.g. Ca^{2+} in water) or in a compound (e.g. Ca^{2+} in calcite). It is easier to determine for ionically bonded compounds (Na^+ and Cl^- in halite), but even in compounds dominated by covalent bonds, oxidation state can be assigned to atoms, e.g. in methane (CH_4), C and H can be indicated as C^{4-} and H^+. Often "valence state" and oxidation state are used synonymously, but it is best to not use the term valence state to indicate oxidation state. You might say that chlorine has seven valence electrons in the neutral state, but in terms of charge you would say that Cl can adopt many oxidation states, e.g. Cl^- (in NaCl), Cl^0 (Cl_2 gas), Cl^{7+} (in the perchlorate anion ClO_4^-), and more. Also according to IUPAC, oxidation states are best represented as e.g. Al^{3+} and O^{2-} (rather than e.g. Al^{+3} and O^{-2}), although it is common to see both used.

Focus Box 1.15

Coulombic Interaction Example

The classic example of Coulombic attraction is the bond between an alkali metal cation (e.g. Na^+) and a halogen anion (e.g. Cl^-). The cation and anion are electrostatically attracted to each other and the result is formation of an ionic bond producing a solid, in this case cubic vitreous crystals of halite (NaCl).

Loss of an electron by sodium and its incorporation into the valence shell of chlorine can be viewed in the sense of a Lewis electron dot diagram (Figure 1.7).

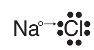

Fig. 1.7 Schematic representation of formation of an ionic bond by transfer of the Na valence electron to Cl. Resulting Na^+ and Cl^- ions form a strong electrostatic attraction. The empty circle next to the Na atom represents the electron lost to the Cl atom.

One way this type of bond forms in the natural world is when evaporation of salty water (e.g. marine water or brines) drives Na^+ and Cl^- concentrations up to levels sufficiently high to allow formation of solid crystals. (More details about the controls on aqueous processes are covered in detail in Chapters 4, 5, and 9.)

the Coulombic interaction between like-charged particles, e.g. 2 cations, causes repulsion).

1.6.2 Determining ionic bond strength

The strength of an ionic bond is largely controlled by the charges on the ions and by the radii of the ions involved in the bonding. This is a concept that should be intuitively apparent because ions with higher charges will be more attracted (provided that they have opposite charges), and the closer the spacing of the ions, generally the stronger the bond.

The attraction of two ions can be quantified by Coulomb's Law:

$$F_c = k \times (q_1 \times q_2)/(\varepsilon \times r) \qquad (1.10)$$

where k is a constant (described below), q_1 and q_2 are the values of ionic charges on the ions, ε is the dielectric constant, and r is the distance between the nuclei of the two ions joined by the bond.

When F_c is negative the ions are attracted; the negative sign indicates that the system (the two ions) have shifted to a lower (more stable) energy state than is the case when the ions are separated. Given that all other terms (k, ε, r) are positive, negative F_c results from two ions with opposite charge, i.e. a cation and an anion.

The constant k is expressed as:

$$k = 1/(4\pi\varepsilon_o) \qquad (1.11)$$

where ε_o is the permittivity constant (sometimes known as P_o or D) – it equals 8.854×10^{-12} $C^2 J^{-1} m^{-1}$ and results in a value for the constant $k = 8.998 \times 10^9$ J·m C^{-2}, where J = joules and C = 1.602×10^{-19} C, a measure of charge.

The dielectric constant ε expresses the effect of the ambient environment on the strength of the bond, the best example being the difference in ionic bond strength in dry air as compared to water. At 20 °C and 1 atm, the *dry air* value for $\varepsilon = 1.0$ whereas the value for ε in *water* at 20 °C = 88. Therefore, all other factors being equal, an ionic bond is 88 times weaker in water than in dry air.

For Na^+ and Cl^- ions, q_1 and q_2 are +1 and −1. The ionic radius of Na^+ in a crystal of NaCl is 1.16Å and the ionic radius for Cl^- is 1.67 Å (where an angstrom is 10^{-10} m). The reason that the Cl^- anion is larger than the Na^+ cation is that Cl^- contains an additional shell of electrons. (In general, anions have larger radii than cations because anions gain electrons when they form ions.)

The bond distance between nuclei will be:

$$1.16 \times 10^{-10}\ \mathrm{m} + 1.67\ \text{Å} \times 10^{-10}\ \mathrm{m} = 2.83 \times 10^{-10}\ \mathrm{m}$$

so the attractive energy of the NaCl bond in air ($\varepsilon = 1.0$) is:

$$\begin{aligned} F_c &= 8.998 \times 10^9\ \mathrm{J{\cdot}m\,C^{-2}} \times (-1.602 \times 10^{-19}) \\ &\quad \times (+1.602 \times 10^{-19}) \div 2.83 \times 10^{-10}\ \mathrm{m} \\ &= -8.15 \times 10^{-19}\ \mathrm{J} \end{aligned}$$

Note that units of charge in the numerator (C^2, Coulombs squared) cancel with C^2 units from the constant, and also that m (meters, from ionic radius r) in the denominator cancel with m in the numerator leaving us with units of J (joules), which express energy lost (if $J < 0$) or gained (if $J > 0$), where negative values indicate transition to a more stable state.

This calculation applies to a single Na–Cl atom pair. If we wished to compute this for a mole we would multiply the result by Avogadro's number (1 mol of NaCl would contain 6.022×10^{23} atoms each of Na and Cl):

$$\begin{aligned} &8.15 \times 10^{-19}\ \mathrm{J/atom} \times 6.022 \times 10^{23}\ \mathrm{atoms\ mol^{-1}} \\ &\quad = 4.91 \times 10^5\ \mathrm{J\ mol^{-1}} = -491\ \mathrm{kJ\ mol^{-1}} \end{aligned}$$

If we compare this to the bond between K^+ (ionic radius = 1.52 Å) and Cl^-, a bond that results in formation of KCl (sylvite or potassium chloride), we find that:

$$\begin{aligned} F_c &= 8.998 \times 10^9\ \mathrm{J{\cdot}m\,C^{-2}} \times (-1.602 \times 10^{-19}) \\ &\quad \times (+1.602 \times 10^{-19}) \div 3.19 \times 10^{-10}\ \mathrm{m} \\ &= -7.23 \times 10^{-19}\ \mathrm{J} \end{aligned}$$

and

$$\begin{aligned} &-7.23 \times 10^{-19}\ \mathrm{J/atom} \times 6.022 \times 10^{23}\ \mathrm{atoms\ mol^{-1}} \\ &\quad = 4.35 \times 10^5\ \mathrm{J\ mol^{-1}} = -435\ \mathrm{kJ\ mol^{-1}} \end{aligned}$$

Considering the attraction of cation and anion, NaCl forms a stronger bond than KCl because the smaller ionic radius of Na allows the Na and Cl nuclei to be held closer.

In the case of magnesium chloride ($MgCl_2$), the ionic charge on Mg is 2+ and its ionic radius in $MgCl_2$ is 0.86 Å. So in this case,

$$\begin{aligned} F_c &= 8.998 \times 10^9\ \mathrm{J{\cdot}m/C^2} \times (-1.602 \times 10^{-19}) \\ &\quad \times (2 + \times 1.602 \times 10^{-19}) \div 2.53 \times 10^{-10}\ \mathrm{m} \\ &= -1.82 \times 10^{-18}\ \mathrm{J} \end{aligned}$$

and

$$\begin{aligned} &-1.82 \times 10^{-18}\ \mathrm{J/atom} \times 6.022 \times 10^{23}\ \mathrm{atoms\ mol^{-1}} \\ &\quad = 1.10 \times 10^6\ \mathrm{J\ mol^{-1}} = -1100\ \mathrm{kJ\ mol^{-1}} \end{aligned}$$

Based on Coulombic attraction, the higher charge and smaller radius of Mg^{2+} compared to K^+ and Na^+ make the $MgCl_2$ lattice energy approximately twice that of KCl and NaCl.

For ionic solids in water ($\varepsilon = 88$ in the denominator), the lattice energies of NaCl, KCl, and $MgCl_2$ are 5.58, 4.95, and 12.5 kJ mol^{-1}, respectively, which is a quantitative way of saying that ionic bonds are approximately two orders of magnitude weaker in water than in dry air.

The treatment presented above only considers the attraction between two ions and does not consider other factors associated with the strength of ionic bonds, two of which include (i) the effect of other ions and the geometry of the lattice structure (this can be assessed using the Madelung constant, which is not covered here), and (ii) temperature; for example, melting points for NaCl, KCl, and $MgCl_2$, respectively, are 801, 770, and 714 °C, differences which are not explained by Coulomb's Law.

1.6.3 Covalent bonding

Covalent bonds involve overlap of electron orbitals, i.e. they are bonds that form by sharing electrons between atoms. Unlike ionic bonding, where atoms have very different attractions to their respective valence electrons, atoms that form covalent bonds have similar attractions to their valence electrons; therefore, because their valence electrons are attracted to their nuclei with similar strength, it

Focus Box 1.16

Covalent Bonding: Diatomic Gas Example

A classic example of covalent bonding involves the attraction of atoms in the diatomic gases H_2, N_2, and O_2. When two oxygen atoms combine to form O_2, there is clearly no difference in the valence electron configuration or in the attraction of each oxygen atom for its electrons. The atoms are effectively equal in structure, so the solution to the octet rule for O_2 involves reorganization and overlapping of electrons to produce valence shells that each contain eight electrons (Figure 1.8).

Both O atoms have satisfied the octet rule the same way, by overlapping electron orbitals to produce a stable configuration. So, while each O atom has six valence electrons, two of them are shared with the adjacent O atom by orbital overlap to produce a strong chemical bond. In this case the bond between the oxygen atoms is a *double bond* because it involves two pairs of electrons, as contrasted to a typical *single bond* that involves only one pair of electrons (refer to the water molecules shown in Figure 1.11).

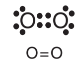

Fig. 1.8 Lewis electron dot diagram of an oxygen molecule (O_2) shown using two different notations. Note double bond between oxygen atoms consisting of two electron pairs depicted by the double dashed lines in the lower example.

is impossible for one atom to lose its valence electron(s) to another atom to form a bond.

Covalent bonds occur between elements with identical or similar electronegativities (Figure 1.9), including the diatomic gases, between H and O in H_2O, between C and O in CO_2, and Si and O in SiO_2. Chemical bonds that are a mix of ionic and covalent (e.g. SiO_2) are termed polar covalent bonds.

1.6.4 Electronegativity and predicting bond type

Electronegativity is a measure of the attraction of a nucleus for its valence electrons. Na and K have low electronegativities because they readily lose their valence electron to satisfy the octet rule, resulting in +1-charged cations. Conversely, fluorine and chlorine have strong attractions to the electrons in their valence shell and furthermore have the ability to pull valence electrons away from nearby atoms to form −1-charged anions and satisfy the octet rule – these elements have high electronegativity values. Electronegativity is important because it helps to predict the type of chemical bond that will form between elements – elements with large differences in electronegativity form dominantly ionic bonds, whereas elements with low differences in electronegativity form covalent or polar covalent bonds.

Figure 1.9 presents electronegativities of the elements and Figure 1.10 shows the % ionic character of

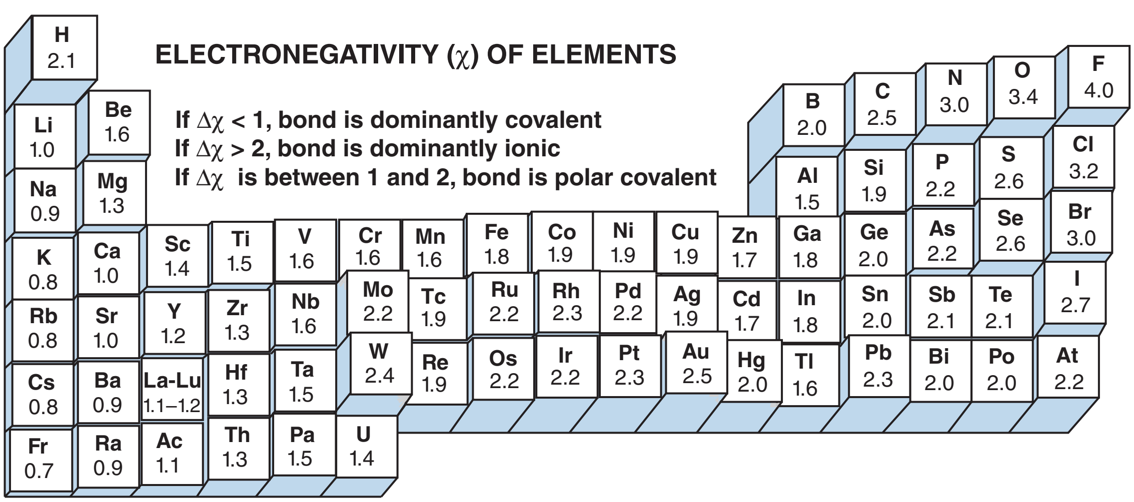

Fig. 1.9 Electronegativity of elements based on Linus Pauling's early twentieth-century research.

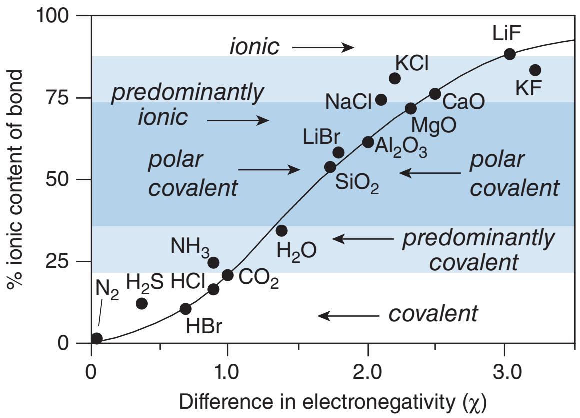

Fig. 1.10 Plot of relationship between difference in electronegativity of two atoms in a bond and the percent ionic character of the bond. Note that no bond shown here is 100% ionic; however, diatomic gases (e.g. N_2, Cl_2, O_2) and the C-C bonds in diamond are 100% covalent. Based on the early and middle twentieth-century work of Linus Pauling and more recent research by Lu et al. (2006).

some selected chemical bonds expressed by difference in electronegativity. Nearly all bonds involving atoms of two elements (i.e. not including diatomic gases like H_2 or O_2 native elements such as Au or Ag) involve some aspect of electron transfer (ionic character) and orbital overlap (covalent character) – the greater the difference in electronegativity, the greater the ionic character (and usually, the greater the tendency to dissociate and dissolve in water).

The electronegativity difference ($\Delta\chi$) for NaCl is 3.0 (Cl) – 0.9 (Na) = 2.1, resulting in a predominantly ionically bonded compound. For a purely covalent molecule like N_2, $O_{2,}$ $Cl_{2,}$ or diamond (pure C), $\Delta\chi$ is zero. Methane (CH_4) and hydrogen sulfide (H_2S) are strongly covalent ($\Delta\chi = 0.4$ and 0.5, respectively). SiO_2 is a mix of covalent and ionic (Figure 1.10) and the term *polar covalent bond* (or *polar bond*) is used to describe this type.

$CaCO_3$ (calcium carbonate, e.g. the mineral calcite) contains bonds between Ca–O and C–O. The Ca–O bonds are predominantly (~70%) ionic ($\Delta\chi = 3.4–1.0 = 2.4$), whereas the C–O bond is predominantly (~80%) covalent ($\Delta\chi = 3.4–2.5 = 0.9$). Understanding this concept is important when predicting solubilities of minerals; for example, in water, calcite dissolves to produce Ca^{2+} ions and the polyatomic $CO_3{}^{2-}$ anion in solution (see Chapter 5 for details of carbonate geochemistry). The covalent character preserves the C–O bond and the carbonate anion ($CO_3{}^{2-}$) is a common constituent of natural waters.

1.6.5 Metallic bonds, hydrogen bonds, and van der Waals forces

Metallic bonds occur among metals such as Cr, Cu, Fe, Ni, and Zn in solid molecules, but unlike ionic or covalent bonds, once valence electrons are released by a metal atom, they are not fixed with a specific atom, but rather migrate through the crystal structure. This type of bond occurs in sulfide minerals such as pyrite, and also in native elements such as Cu, gold (Au), and silver (Ag). These bonds are weaker than covalent and ionic bonds and are part of the reason why metal-bearing sulfide minerals are relatively unstable at the Earth surface.

Dipole bonds, also known as *van der Waals* bonds (and sometimes called van der Waals *forces*), exist between electrically neutral molecules or compounds with some unequal distribution of charge. A great example of a dipole bond exists between water molecules. Water is a dipolar compound, with a positively charged pole and a negatively charged pole (remember that the molecule as a whole is neutral). Figure 1.11 presents a schematic sketch of three adjacent water molecules attracted by dipolar bonds – in this case, the bond occurs between hydrogen atoms at the positively charged pole (δ^+) of water molecules and the negatively charged pole (δ^-) produced by valence

Focus Box 1.17

Ionic vs. Covalent Compounds

NaCl and SiO_2 serve as good examples of the differences between solids dominated by ionic bonds and those dominated by polar covalent bonds. Ionically bonded halite is highly soluble in water, but quartz in very insoluble, helping to explain the common occurrence of quartz sand beaches – if the covalent bonds in quartz were readily destroyed by water we would have no sandy beaches. In fact, we probably wouldn't have mountains or canyons either, for the strong bonds in rock-forming minerals are primarily polar covalent. In the absence of water, ionic bonds and covalent bonds are generally both strong, and appreciably stronger than the other types of chemical bonds in nature such as metallic bonds and dipole bonds (e.g. hydrogen bonds, van der Waals bonds).

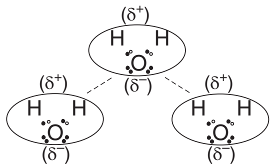

Fig. 1.11 Diagram of three water molecules showing polarity of the water molecule (δ^+, δ^-) as well as hydrogen bonds (dashed lines) between H and O in adjacent molecules. Ovals are used here to highlight the three individual water molecules. The small empty circles between H and O atoms represent electrons from the H atoms; the solid circles represent electrons from oxygen atoms.

electrons from the highly electronegative oxygen atom in the adjacent water molecule.

This specific type of dipolar bond is known as a *hydrogen bond*, and although shown between adjacent H_2O molecules in this case, hydrogen bonds can also occur between H and O (or N) within a molecule. Note that the dots surrounding the O atoms represent electrons – oxygen satisfies the octet rule by sharing an electron with an electron from each of the H atoms, and the H–O bonds within the H_2O molecules (within the ovals) are single bonds (dominantly covalent) involving one pair of electrons each.

Water has a permanent dipole, but *van der Waals* bonds also exist between electrically neutral molecules or compounds where the electrostatic attractions are temporary, commonly existing as transitory states involving alternating positive and negative charge distributions that minimize repulsion. The example in Figure 1.12 represents two different transitory states of adjacent atoms where the dots are a schematic representation of an electron cloud. The delta symbol (δ^-) represents the side of

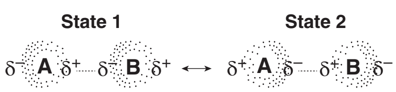

Fig. 1.12 Van der Waals bonds between adjacent atoms. A and B represent nuclei of adjacent atoms and dots are electrons (shown schematically). Note that in the pair of atoms in "State 1," electron clouds are shifted to the left, causing attraction between the opposite poles (δ + and δ-). At a subsequent moment in time ("State 2"), electron clouds are shifted to the right, also enhancing attraction of the atoms. If this type of alternating motion is synchronized, the atoms will be weakly attracted by the van der Waals bonds indicated by the dashed line.

the atom or molecule with the greater concentration of negative charge (Figure 1.12).

While only schematic, this diagram indicates how alternating electron distributions can lead to attraction between adjacent atoms or nonpolar compounds. Both A and B are transitory states, and in fact, both are unstable states – as soon as the electrons take on the configuration represented in A, they are driven in the opposite direction by repulsive forces, causing configuration B. This then drives the electron cloud back toward configuration A, and the alternating transitory states facilitate atomic or molecular attraction. Although these bonds are far weaker than covalent, ionic, or metallic bonds, they are important to understand because they control melting and boiling points of many compounds, particularly nonpolar organic compounds including pesticides, fuels, and solvents.

1.7 ACID–BASE EQUILIBRIA, PH, K VALUES

Chemical reactions in natural systems commonly occur in the presence of water, and understanding acid–base chemistry is crucial to understanding a large proportion of issues in geochemistry, including the solubility of minerals and trace metals, chemical weathering, the decomposition of organic matter, speciation of chemical elements, and reactions in the atmosphere.

1.7.1 Definitions of acids and bases

Following the convention established by the Swedish chemist Svante Arrhenius, an *acid* is a compound that releases hydrogen ions. The dissociated hydrogen ion is often written as H^+, but be aware that H^+ is effectively a proton, and also be aware that the tendency of H^+ to bond to water molecules is why we often see H_3O^+ (the "hydronium ion") used to represent the dissociated proton in solution (i.e. when dissolved in water). A few examples of classic acids are the inorganic acids hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and nitric acid (HNO_3), and organic acids such as formic acid (HCOOH, also known as methanoic acid, which is what an ants stings with) and acetic acid (CH_3COOH also known as ethanoic acid, or more commonly as vinegar).

The Arrhenius definition of a *base* is a compound that, when dissolved in water, releases hydroxyl anions

Focus Box 1.18

Acids in Solution

Nitric acid is a simple example of how acids behave in solution

$$HNO_3 \rightarrow H^+_{(aq)} + NO_3^-{}_{(aq)} \quad (1.12)$$

In water, HNO_3 dissociates to release hydrogen ions (and an equal amount of nitrate anions) into solution. The subscript (aq) is used here to indicate that the ions are dissolved in water (i.e. are aqueous). The extent to which an acid like HNO_3 dissolves determines its strength, and Table 1.3 contains data that allow you to predict this. Weak acids tend to remain undissociated in solution, the result being low amounts of H^+ in solution; the opposite is true for strong acids.

Table 1.3 Selected acids and their Ka values, pKa values, and conjugate bases.

Acid				Conjugate base	
Name	**Formula**	**Ka**	**pKa**	**Formula**	**Name**
Hydroiodic acid	HI	3.2×10^9	−9.5	I^-	Iodide
Hydrobromic acid	HBr	1.0×10^9	−9.0	Br^-	Bromide
Hydrochloric acid	HCl	1.3×10^6	−5.1	Cl^-	Chloride
Sulfuric acid	H_2SO_4	1.0×10^3	−3.0	HSO_4^-	Hydrogen sulfate anion
Hydrogen sulfate ion	HSO_4^-	1.0×10^{-2}	+2.0	SO_4^{2-}	Sulfate
Sulfurous acid	H_2SO_3	1.3×10^{-2}	+1.9	HSO_3^-	Hydrogen sulfite anion
Nitric acid	HNO_3	2.4×10^1	−1.4	NO_3^-	Nitrate
Phosphoric acid	H_3PO_4	7.1×10^{-3}	+2.2	$H_2PO_4^-$	Dihydrogen phosphate anion
Dihydrogen phosphate ion	$H_2PO_4^-$	6.3×10^{-8}	+7.2	HPO_4^{2-}	Hydrogen phosphate anion
Hydrogen phosphate ion	HPO_4^{-2}	4.2×10^{-13}	+12.4	PO_4^{3-}	Phosphate anion
Nitrous acid	HNO_2	7.2×10^{-4}	+3.1	NO_3^-	Nitrite anion
Hydrofluoric acid	HF	6.8×10^{-4}	+3.2	F^-	Fluoride
Methanoic (formic) acid	HCOOH	1.8×10^{-4}	+3.7	$HCOO^-$	Methanoate (formate) anion
Benzoic acid	C_6H_5COOH	6.3×10^{-5}	+4.2	$C_6H_5COO^-$	Benzoate anion
Ethanoic acid	CH_3COOH	1.8×10^{-5}	+4.7	$CH_3COO–$	Ethanoate (acetate) anion
Carbonic acid	H_2CO_3	4.4×10^{-7}	+6.4	HCO_3^-	Bicarbonate
Hydrogen carbonate ion	HCO_3^-	4.7×10^{-11}	+10.3	CO_3^{2-}	Carbonate anion
Hydrogen sulfide	H_2S	1.1×10^{-7}	+7.0	HS^-	Hydrogen sulfide anion
Ammonium ion	NH_4^+	5.8×10^{-10}	+9.2	NH_3	Ammonia

(OH^-) in solution. A few classic examples of bases are sodium hydroxide (NaOH), calcium hydroxide ($Ca[OH]_2$), and ammonium hydroxide (NH_4OH). In solutions, bases behave as follows:

$$NaOH = Na^+_{(aq)} + OH^-_{(aq)} \quad (1.13)$$

Strong bases – like strong acids – dissociate completely, or nearly so. A strong base like NaOH may almost completely dissolve in solution, producing a high concentration of hydroxyl anions, thus producing a very basic solution. A weak base like NH_4OH (ammonium hydroxide) is much less soluble, so in solution it produces a much lower concentration of OH^-. Similarly, the mineral acids listed above are strong acids, while the organic acids (formic and acetic acid) are relatively weak and produce much lower concentrations of H^+ in solution.

Two additional definitions of acids and bases include Brønsted and Lewis classifications.

A *Brønsted acid* is a substance that can donate a proton (i.e. H^+) to another substance, and a *Brønsted base* is a substance that can accept a proton from another substance. The following chemical reaction illustrates this

Focus Box 1.19

Defining pH

The pH scale is the conventional means of expressing the acidity or alkalinity of a solution. The concentration[a] of H^+ ions in solution defines pH according to the equation

$$pH = -\log[H^+] \quad (1.14)$$

where $[H^+]$ is the concentration of hydrogen ions in solution, in mol l^{-1}. In a highly acidic solution with 10^{-2} mol l^{-1} of H^+, the pH = 2. In an alkaline solution with 10^{-11} mol l^{-1} of H^+, the pH = 11. In aqueous solutions, the product of the concentrations of H^+ and OH^- is 10^{-14} ($[H^+] \times [OH^-] = 10^{-14}$). What this translates to is that if the concentration of $H^+ = 10^{-4}$, the concentration of $OH^- = 10^{-10}$. In this case, pH = 4 and qualitatively, it makes sense that the solution is acidic because there is far more H^+ than OH^-. In an alkaline solution with $[OH^-] = 10^{-2}$, the concentration of $[H^+] = 10^{-12}$ and the pH = 12.

[a]Note: this section discusses aqueous species (e.g. H^+, NO_3^-) in terms of concentration (e.g. $[NO_3^-]$), yet often species in solution are represented by activity $a(NO_3^-)$, a term which takes into account effects of other ions in solution on the effective concentration (often activities are less than actual concentrations). In this introductory section and in many other resources, concentrations are used; Chapter 4 (Section 4.6) discusses the concept of activity relative to concentration.

relationship:

$$HCl + NH_3 = Cl^- + NH_4^+ \quad (1.15)$$

where HCl (the Brønsted acid) donates a proton that is accepted by the Brønsted base NH_3 (ammonia). The result is formation of a chloride anion and ammonium, where Cl^- can be termed a Brønsted base (it can accept a proton) and NH_4^+ is considered a Brønsted acid. Most *minerals* can be viewed as Brønsted bases because they consume H^+ when they undergo chemical weathering in soils. A good example is the weathering of gibbsite, $Al(OH)_3$, in acidic soils:

$$Al(OH)_3 + 3\,H^+ \rightarrow Al^{3+} + 3\,H_2O \quad (1.16)$$

Consider also that NaOH, described as an Arrhenius base above because it yields dissolved OH^- in solution, is also considered a base by the Brønsted definition:

$$NaOH + H^+ \rightarrow Na^+ + H_2O \quad (1.17)$$

Lewis acids are substances that can accept electron pairs when forming bonds (H^+ is a good example), whereas *Lewis bases* are electron pair donors (OH^- is a good example of this type of substance).

1.7.2 The law of mass action and quantifying acid dissociation

Consider now the dissociation of two acids, one a strong acid (nitric acid, HNO_3) and one a relatively weak acid (carbonic acid, H_2CO_3).

$$(1)\ HNO_3 \rightarrow H^+ + NO_3^- \quad (1.18)$$

$$(2)\ H_2CO_3 \rightarrow H^+ + HCO_3^- \quad (1.19)$$

The *Law of Mass Action* quantifies the dissociation of nitric acid as follows:

$$Ka_{HNO3} = [H^+] \times [NO_3^-] \div [HNO_3] = 10^{-1.3} \quad (1.20)$$

The concentrations of H^+ and NO_3^- are equal when HNO_3 dissolves and if we assume a HNO_3 concentration of 1 mol l^{-1}, $[H^+] = [NO_3^-] = \sqrt{10^{-1.3}} = 0.22$ or 2.2×10^{-1} mol l^{-1}.

The same treatment for carbonic acid produces:

$$Ka_{H2CO3} = [H^+] \times [HCO_3^-] \div [H_2CO_3] = 10^{-6.37} \quad (1.21)$$

If, like was done with HNO_3, we assume an H_2CO_3 concentration of 1 mol l^{-1}, $[H^+] = [HCO_3^-] = \sqrt{10^{-6.37}} = 6.5 \times 10^{-4}$ mol l^{-1}. In other words, the concentration of H^+ produced by nitric acid dissociated in water is approximately one thousand (10^3) times greater than H^+ produced by an equivalent amount of carbonic acid in water.

K_a values for some relatively common acids are presented in Table 1.3.

1.8 FUNDAMENTALS OF REDOX CHEMISTRY

Reduction–oxidation (redox) chemistry refers to processes that take place when atoms gain or lose electrons, and often involves reactions where O_2 is a reactant or product. Electron transfer facilitates exchange of energy that is crucial to processes across the chemical spectrum, from aquifer and soil dynamics to photosynthesis and degradation of toxic organic compounds. In nature, redox reactions often involve changes to the oxidation state of elements like carbon, nitrogen, oxygen, sulfur, manganese, and iron that can exist in different oxidation states (e.g. carbon exists in many oxidation states, including C^{4-}, C^0, C^{2+}, C^{4+}), where the change from one oxidation state to another involves gain or loss of electrons. Electron transfer associated with redox reactions is energy for microbial organisms, so when we think about redox reactions, we must consider the potential influence of microbial activity.

1.8.1 Defining oxidation and reduction

Oxidation refers to the loss of electrons by an atom. Two common examples are the oxidation of iron from its ferrous state (Fe^{2+}) to its ferric state (Fe^{3+}) by loss of one electron, and of nitrogen from N^{3+} to N^{5+} by loss of two electrons. These two reactions are represented as follows:

$$Fe^{2+} = Fe^{3+} + e^- \qquad (1.22)$$

$$N^{3+} = N^{5+} + 2e^- \qquad (1.23)$$

Where do those liberated electrons go? They probably were pulled away from the oxidized atom because a neighboring atom had a greater attraction for those valence electrons. The oxidation of one atom cannot occur without a corresponding change to another atom. This change is *reduction* and it takes place when an atom gains electrons.

Two common examples are the reduction of oxygen gas (where the oxidation state of oxygen is O^0) to oxygen anions (O^{2-}), and of C^{4+} (e.g. the C in CO_2 and $CaCO_3$) to molecular carbon, C^0 (e.g. the oxidation state of C in some forms of organic matter).

$$O_2 + 4e^- = 2O^{2-} \qquad (1.24)$$

$$C^{4+} + 4e^- = C^0 \qquad (1.25)$$

1.8.2 Redox reactions

While it is useful to examine individual examples of reduction or oxidation, loss of electrons from one atom results in gain of electrons for another atom. A simple example is the oxidation of iron metal (Fe^0) to iron oxide (Fe_2O_3) where Fe occurs in its trivalent or ferric state (Fe^{3+}).

$$4Fe^0 + 3O_2 = 2Fe_2O_3 \qquad (1.26)$$

Examining individual reduction and oxidation pairs helps to see where and how the exchange of electrons takes place:

$$Fe^0 = Fe^{3+} + 3e^- \qquad (1.27)$$

$$\tfrac{1}{2}\,O_2 + 2e^- = O^{2-} \qquad (1.28)$$

All elements in their pure state, like the Fe atom and O atom (represented as $\tfrac{1}{2}\,O_2$) shown above, have an oxidation state of zero.

The oxidation of iron metal (Fe^0) by oxygen gas (O_2) involves the loss of three electrons from a neutral iron atom and gain of two electrons by a neutral oxygen atom. Clearly, one oxygen atom cannot cause the oxidation of one iron atom from Fe^0 to Fe^{3+}, and this brings up the need to balance redox reactions, as follows:

$$2 \times (Fe \rightarrow Fe^{3+} + 3\,e^-)$$

$$3 \times (\tfrac{1}{2}\,O_2 + 2\,e^- \rightarrow O^{2-})$$

This results in a balanced pair of reactions (with respect to electrons) where two iron atoms lose a sum of six electrons and three oxygen atoms gain a sum of 6 electrons:

$$2\,Fe \rightarrow 2\,Fe^{3+} + 6\,e^-$$

$$1.5\,O_2 + 6\,e^- \rightarrow 3\,O^{2-}$$

. . . and the paired redox reaction can be expressed as:

$$2\,Fe + 1.5\,O_2 \rightarrow 2\,Fe^{3+} + 3\,O^{2-} \qquad (1.29)$$

The electrons are excluded from this redox reaction because there are 6 e^- on both sides (products and reactants) and thus cancel each other out, yet *electron flux is implied by the change in oxidation states of Fe and O atoms*. Terminologically, iron is the reducing agent that donates electrons to oxygen, causing oxygen to become reduced (and iron to be oxidized); oxygen is the oxidizing agent that pulls electrons from iron, which results in reduction of oxygen and oxidation of iron. In reality, the oxidation of iron ends up producing iron oxide, shown here as the mineral hematite:

$$2\,Fe + 1.5\,O_2 \rightarrow Fe_2O_3 \qquad (1.30)$$

Hematite consists of Fe in its most oxidized state (Fe^{3+}, ferric iron) and oxygen in the form that it takes in virtually all compounds, O^{2-}.

Redox chemistry comprises some of the most important reactions in the realm of geochemistry and biochemistry. Microbial activity often plays an important role in redox chemistry because electron transfer is an energy source – a classic example is the microbially mediated decomposition

Focus Box 1.20

"Oxidizing" or "Oxidized"? "Reducing" or "Reduced"?

This is a question of terminology. In effect, the terms "oxidizing" and "oxidized" are synonymous. An oxidized soil will likely contain abundant available O_2 as well as minerals that are stable in an oxidized (or oxidizing) environment, e.g. iron oxides. This soil will be an oxidizing environment because if a chemically reduced substance like an organic compound or sulfide were to be transported into the soil, an oxidation reaction would likely lead to decomposition of the reduced substance. Similarly, "reduced" and "reducing" environments are effectively synonymous. The terms can also be viewed in this way: "oxidizing" and "reducing" are often used to describe the environment whereas "oxidized" and "reduced" might be more likely to be used for species or elements, as in "Is the iron in an oxidized or reduced state in that part of the aquifer?"

of fuels and solvents in soils, where the oxidation of organic carbon provides energy to the microbe and results in the transformation of leaked fuel into H_2O and CO_2. Refer to Chapter 3 for organic compounds in the environment, and to Chapter 4 for more on redox reactions and aqueous geochemistry (Sections 4.5 and 4.9).

1.9 CHEMICAL REACTIONS

Reactions among elements and compounds have been presented in a few ways in this chapter thus far, including reference to chemical bonding, the formation of elements, and redox chemistry. Chemical equations are algebraic expressions that represent the masses and charges of constituents involved in chemical reactions, and in some ways are the language of geochemistry, or at least one of the languages. Accordingly, the following section will present a few fundamental concepts about chemical reactions, what they represent, how to balance them, and how to interpret them.

First, a few general rules. Chemical reactions commonly take place in the presence of water, but if water is not produced or is not consumed by the reaction, it is not listed in

Focus Box 1.21

Determining and Balancing Chemical Equations

How to determine a balanced chemical reaction for the combustion of octane: First, knowing that combustion is the reaction of a substance with oxygen, you can identify O_2 as a reactant. Looking up the composition of octane (C_8H_{18}, see Chapter 3) gives you the other reactant. Products of hydrocarbon combustion are water and carbon dioxide[a], so knowing reactant and products, the unbalanced equation is:

$$C_8H_{18} + O_2 = H_2O + CO_2$$

Rule #1: Perhaps this goes without saying, but in a balanced chemical equation there must be equal moles (or atoms) of each element on the reactant and product side; in this example, on the reactant side there are 8 mol of C and 18 mol of H (comprising 1 mol of octane), and 2 mol of O (in 1 mol of oxygen gas, O_2).

Rule #2: Always save the single element (in this case, O_2) or the least complex compound for last – it is easiest to adjust at the end.

Step #1: Add coefficients to adjust upward elements that are lacking. In this case, coefficients need to be placed in front of H_2O and CO_2 to raise molar values of H and C on the reactants side – to balance H, we need 9 mol of H_2O (i.e. 18 mol of H), and to balance C, we need 8 mol of CO_2 (equal to 8 mol of C).

Step #2: This gives us an intermediate-stage reaction, i.e.

$$C_8H_{18} + O_2 = 9\,H_2O + 8\,CO_2$$

A quick glance makes it obvious that oxygen is not balanced. The products side now has 9 mol of O from H_2O and 16 mol of O from CO_2.

Step #3: To balance O_2, we need 25 mol of O on the reactants side, which equals 25/2 or 12.5 mol of O_2.

The balanced reaction is: $C_8H_{18} + 12.5\,O_2 = 9\ H_2O + 8\ CO_2$

Equal signs (=) are often used rather than arrows in chemical equations in cases where the reaction is reversible. This is a simple example, but there are others in the end-of-chapter problem set.

([a] Note that in many cases, fuel-rich combustion can also produce carbon monoxide [CO].)

the reaction. Given that the First Law of Thermodynamics states that matter can neither be created nor destroyed, but rather can only change forms, chemical reactions should not give the illusion that the first law is being violated – what this means is that all chemical reactions must be balanced. If there are four oxygen *atoms* (or moles of oxygen) expressed on the reactants side of the equation, then there also must be four oxygen *atoms* (or moles of oxygen) on the products side. Similarly, if the reaction is of the redox variety, the charges (sum of + and −) should be equal on both sides. If the reaction involves nuclear fusion or fission, then energy and mass should be equal on both sides of the equation.

1.10 EQUILIBRIUM, THERMODYNAMICS, AND DRIVING FORCES FOR REACTIONS: SYSTEMS, GIBBS ENERGIES, ENTHALPY AND HEAT CAPACITY, ENTROPY, VOLUME

1.10.1 Pyrite oxidation as an introductory example

This treatment of thermodynamics begins with the example of pyrite (FeS_2 or iron disulfide), a mineral that forms in O_2-poor systems (reducing environments) that include deep crustal levels and anoxic surface environments like swampy muds (technically iron sulfide that forms at earth surface temperatures is a poorly ordered form of ~ FeS, e.g. mackinawite). Iron, in the Fe^{2+} state, and sulfur, in a combination of S^{2-} and S^0 states (average = S^-), both occur in chemically reduced forms in the mineral pyrite – these oxidation states are stable in reducing/anoxic/anaerobic/O_2-poor environments.

Given the conditions under which pyrite forms, it is possible to predict its fate in oxidizing (O_2-rich) environments, common examples being soils exposed to the oxygen-rich, water vapor-bearing atmosphere, or an O_2-rich bubbling stream, where the stable forms of iron and sulfur are Fe^{3+} and S^{6+}. Under oxidizing conditions, pyrite undergoes (bio)chemical oxidation, producing iron hydroxide with its characteristic rusty orange stains typical of many rock outcrops and soils. The reaction of pyrite, water, and oxygen to produce iron hydroxide, sulfuric acid, and free electrons (oxidation!) can be expressed as follows:

$$2FeS_2 + 7H_2O + {}^{15}/_2O_2 \rightarrow 2Fe(OH)_3 + 4H_2SO_4 \tag{1.31}$$

(In reality this reaction occurs in two or more steps, often in the presence of sulfur-oxidizing bacteria). Viewing this reaction in terms of the extent of iron oxidation would likely result in a characteristic pattern observed for many reactions in nature (Figure 1.13).

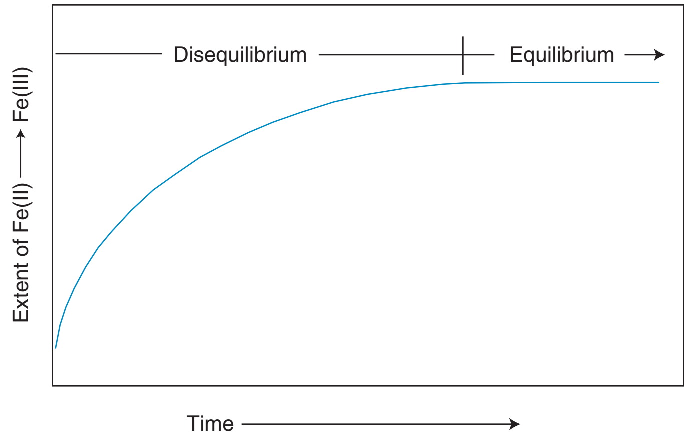

Fig. 1.13 Typical progression of a geochemical system toward equilibrium. A high degree of disequilibrium in the early stages causes rapid rates of change, but as the system approaches equilibrium, rates decrease logarithmically.

In Figure 1.13, the initial system (pyrite in contact with atmosphere) is out of equilibrium – both the Fe and S are unstable in reduced forms when exposed to O_2-rich air (e.g. by a landslide that exposes fresh unoxidized rock) and the pyrite begins to react. This reaction is expressed as $Fe(II) \rightarrow Fe(III)$ in the graph, and note that initially the reaction occurs rapidly but as the reaction progresses the rate steadily decreases and ultimately ceases altogether. There are two probable explanations:

1 the system has reached *equilibrium*, a condition where net concentrations of products and reactants do not change. *Dynamic equilibrium* sometimes occurs in natural systems, when the rate of formation of products equals the rate of formation of reactants. If the $Fe(OH)_3$ and H_2SO_4 produced by pyrite oxidation are not leached out of the system, a dynamic equilibrium may be established where the rate of the forward reaction shown above is equal to the rate of the reverse reaction – i.e. FeS_2, O_2, and H_2O are produced at the same rate as are $Fe(OH)_3$ and H_2SO_4. At dynamic equilibrium, reactions are taking place, namely "products" are dissolving to produce "reactants" at the same rate that "reactants" produce "products," but the net concentrations of products and reactants do not change with time. However, any change to a variable involved in a dynamic equilibrium (e.g. concentration of reactant or product, volume, pressure, temperature) will cause a shift to counter the change. For example, loss of a reactant (e.g. burial under a subsequent landslide and water-logging limits exposure to O_2) will shift the reaction toward the direction of reactants – the rate will slow, or reactants will be produced at the expense of products. Or, if products are lost from the system (e.g. soluble H_2SO_4 is leached away), the reaction will continue to form products, which leads to the other possibility:

2 The reaction has run to completion. In some natural systems, where products are lost due to leaching (e.g. of H_2SO_4 in the case above) or degasification (e.g. of CO_2 with dissolution of carbonates), a dynamic equilibrium cannot be established. If the pyrite reaction above stopped because all Fe(II) had been consumed to produce Fe(III) (i.e. if the reaction were to run to completion because products are being lost from the system), that system will not reach dynamic equilibrium. The natural environment differs from the laboratory in that reactants are often lost from soils, rocks, and ground waters, and dynamic equilibrium may not apply. (In this case, we might use the term *steady state* to describe the static condition.) In other cases, reactions in nature may not reach equilibrium because reaction rates are very slow – the reaction never proceeds past the early convex part of the disequilibrium curve. This often occurs in soils, where igneous minerals such as amphiboles and pyroxenes that are stable in high-temperature, low-O_2 environments persist in a state of disequilibrium because the rates at which they decompose in weathering environments are relatively slow.

1.10.2 Systems, species, phases, and components

In spite of certain limitations, examining environmental systems through the lens of *equilibrium thermodynamics* can be very useful. It can help determine the direction in which chemical changes will take place (e.g. pyrite is unstable and will oxidize in contact with the atmosphere) and also to infer rates because the farther a system is from equilibrium, the faster it will react to reach equilibrium. A common term used in thermodynamics is *system*, which is a somewhat arbitrary definition of the components we wish to consider. Depending on the question, a system might be an aquifer, or a pore within an aquifer, or the entire hydrologic cycle; it could be an entire granitic pluton, or it might be a micron-sized fluid inclusion in a quartz crystal. It really depends on the scale of study. If the question is climate change, the entire troposphere might be considered as the system, or a smaller system comprised only of a landfill might be defined as the system if the main concern is a single source of carbon (e.g. CH_4).

In geochemistry, *species* are microscopic entities, commonly ions or gases such as Ca, CO_3^{2-}, SO_4^{2-}, CO_2, or H_2S, whereas *phases* are physically separable parts of a system, typically minerals, liquids (e.g. H_2O), and distinct gases (dissolved CO_2 and O_2 in stream water, for example). Phases are comprised of species – for example, the *phase* calcite is comprised of the *species* Ca^{2+} and CO_3^{2-}, or of the *species* CaO and CO_2 (calcite can be defined in either way). While species are generally substances than can or do exist in nature, *components* do not necessarily exist in nature. Sometimes they are similar to species, but in other cases they may be mathematical expressions useful in thermodynamic calculations, one example being KNa_{-1}, a mathematical operator used to indicate gain of K and loss of Na (e.g. by substitution in a phase such as smectite – refer to Chapter 2, Section 2.4.1). So, a soil with the mineral dolomite ($CaMg[CO_3]_2$), water, dissolved Ca^{2+}, dissolved Mg^{2+} and CO_3^{2-}, CO_2 gas, and quartz could be defined as having four phases (dolomite, water, quartz, CO_2 gas) and 6 species or components (Ca^{2+}, Mg^{2+}, CO_3^{2-}, CO_2, H_2O, and SiO_2).

Lastly, the *phase rule* (sometimes referred to as *Gibbs'* phase rule) relates components (C), phases (P), and degrees of freedom (F) according to this simple equation:

$$F = C - P + 2 \tag{1.32}$$

Degrees of freedom represent tangible changes to a system, typically temperature and pressure. In a system with 2 degrees of freedom, temperature and pressure can both

Focus Box 1.22

What is a "System" in Geochemistry?

Systems can be *open* (e.g. a stream, the atmosphere, a leaking landfill), where material is added or lost, or *closed*, where flow of material is restricted (e.g. tiny pores within impermeable fine-grained sediments, and where chemical reactions can be modeled with no gain or loss of elements). In some cases, systems are closed with respect to solids but open with respect to gases or heat, and in other cases systems can be defined as closed to physical and thermal flux, in which case they are *isolated*. Systems are comprised of components, phases, and species.

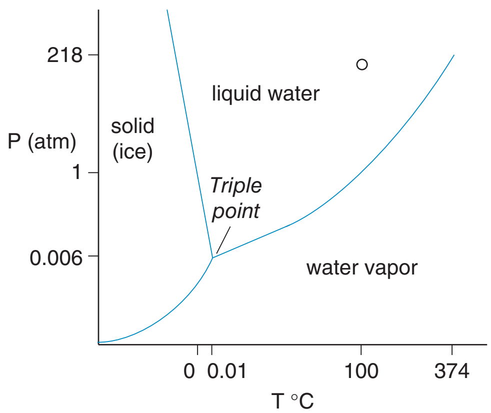

Fig. 1.14 Phase diagram for H_2O depicting one component (H_2O) and three phases (solid, liquid, and gaseous water). The circle in the upper right is plotted at 100 °C and 200 atm pressure, an example of a point where there exist two degrees of freedom.

change without producing a change in the state of the system. The classic example involves a simple system involving only one component, H_2O, which can exist in three phases (solid, liquid, and vapor forms of H_2O), as displayed in the H_2O phase diagram (Figure 1.14).

There is one point in the H_2O phase diagram where all three phases coexist – the triple point. At the triple point, there is one component (H_2O; $C = 1$) and three phases (solid, liquid and vapor; $P = 3$). The phase rule indicates that for this system,

$$F = 1 - 3 + 2 = 0$$

In other words, there are no degrees of freedom. Any change in either T or P will produce a change in the state of the system; for example, increasing T at constant P will cause ice to melt and liquid to vaporize. Increasing P at constant T will cause vapor to condense and ice to melt, producing a system with only one phase. Consider for a moment a system with only one phase, liquid water at 100 °C and 200 atm of pressure (indicated by the circle in Figure 1.14). In this case, the phase rule indicates that (for a system where $C = 1$ and $P = 1$) there will be two degrees of freedom, and this is borne out in the diagram – if either T or P changes, or even if both T and P simultaneously change, there will be no change to the state of the system. It will remain liquid water until the system either cools or decreases in pressure to the point where P-T reaches the phase boundary (line) between liquid and solid or between liquid and vapor.

1.10.3 First law of thermodynamics

The term thermodynamics implies an approach based on changes in *heat*, and the field did originate in studies of the transformation of heat energy to mechanical energy during the 1800s, much of it related to the industrial revolution. Energy can change forms, e.g. *potential energy* to heat (or vice versa), as in the combustion of organic matter, a process where *stored chemical potential energy* is converted to heat energy. Thermodynamics deals with transfers of energy, and one of the fundamental principles is the

Focus Box 1.23

Example of Heat, Work, and Systems

Consider an experiment you could perform while sitting in your overstuffed chair while reading this book. This experiment will illustrate the example of heat (Q) produced by the work (W) of rubbing hands together. The system can be defined as your body and its immediate surroundings. The energy you need to move your shoulders and arms to produce friction comes from the stored energy in the chemical bonds in the food you recently ate, and in a simplified approximation, this chemical energy is transformed to mechanical energy. The friction between your hands converts mechanical energy to heat energy, causing your hands to warm up (and raising the temperature of the system). This heat will soon be lost to the surroundings (an issue to be addressed with the Second Law), but if we consider the net energy of the system (body and immediate surroundings), it has not increased or decreased, but rather merely has changed forms. Of course, the heat will eventually escape from your surroundings and ultimately you will need to eat more food to provide the chemical energy needed to reinitiate the cycle (conversion of chemical energy in food to heat energy is an irreversible reaction in our bodies). In terms of the equation of the First Law, the work (W) done will have a positive sign, as will the heat term Q (heat is gained by the system, so the term Q will have a positive sign, because in geochemistry, the flow of heat is considered positive for any system that gains heat). So, in a semi-quantitative sense, W and Q will both be positive and the values will be equal, and $\Delta E = Q - W = 0$, reflecting the fact that there is no change in the net energy of our body and its surroundings (at least in the short term).

First Law of Thermodynamics, often known as the *Law of Conservation of Matter and Energy*, which can be stated as follows:

$$\Delta E = Q - W \tag{1.33}$$

Or, for small increments of change, this equation can be stated as:

$$dE = dq - dW \tag{1.34}$$

E is the *internal energy* of a system, Q or dQ represent *heat* flux, and W represents *work* done on the system. The first law essentially states that energy is neither created nor destroyed – matter and energy may change forms, new phases may be produced, gases may convert to solids, or solids may dissolve, but the net energy of a closed system never changes (or, for an open system, the net energy of the open system and its surroundings never changes). The kinetic energy of friction along a geological fault may produce heat, or the chemical potential energy stored in the covalent bonds in hydrocarbons may release heat during combustion, but the net change in energy is zero.

Work can be defined as follows:

$$dw = P \times dV \tag{1.35}$$

where P is external *pressure* on a system and dV is the change in *volume* of the system. A typical way to consider work relative to volume is to quantify the work done by expansion during the change of state from liquid water to water vapor. At constant P, a positive dV term (expansion increases V) will produce a positive dw, indicating that work has been done on the surroundings by the system. If you substitute the PdV term for W into Eq. (1.34) of the first law, you will arrive at this equation for the first law, expressed in terms of change in *internal energy*:

$$dE = dq - PdV \tag{1.36}$$

1.10.4 Second law of thermodynamics

The *Second Law of Thermodynamics* deals with *entropy,* a measure of the degree of *disorder* within a system. Any system tends toward a state of increasing randomness unless energy is added to the system to increase order. Increasing entropy is a *spontaneous* process and energy must be added to produce order. In geochemistry, an example of entropy as a spontaneous process is chemical weathering of a basalt, for example, where minerals with ordered crystal lattice structures (a low entropy state) are decomposed into soluble aqueous species such as Na^+, Ca^{2+}, and $Si(OH)_4$ that are then scattered across the globe. Only with addition of energy (e.g. the internal heat of the earth) can some order be restored (i.e. entropy decreased). An everyday example of entropy is this: the natural state of a kitchen or living room will progress toward a state of disorder (greater entropy) characterized by dirty dishes, potato chip bags, music scores, and old newspapers scattered about unless we expend energy to restore order.

Entropy (S) can be represented by the following equation, where q is heat and T is temperature and the process is reversible:

$$dS = dq/dT \tag{1.37}$$

Entropy can be quantified in terms of change in heat content per change in temperature, and units of S are joules/degree (non-Si units are cal/deg.; 1 cal = 4.18 J). A useful example is to consider the entropy of liquid water compared to water vapor at 25 °C and a pressure of 1 atm (1.01325×10^5 Pascals, or 1.01325 bar). S (entropy) for liquid water (H_2O_l) is 292 cal/mol/deg, and for H_2O_g it is 789 cal/mol/deg (Dean 1979). Intuitively, the value of S is greater for the gaseous, more disordered state of H_2O than for the liquid state.

Focus Box 1.24

Notes on Standard Temperature and Pressure

For thermodynamic data in low-temperature geochemistry (Appendix IV), standard conditions are 25 °C (298.15 K, 77 °F) and 1 atm pressure (1.01325×10^5 Pascals [Pa] or 1.01325 bar) – IUPAC refers to 25 °C and 1 atm as standard ambient temperature and pressure (SATP), consistent with standard values used by the US EPA. The US National Institute of Standards and Technology (NIST) uses 20 °C and 1 atm (often referred to as normal temperature and pressure, NTP) and IUPAC defines standard temperature and pressure (STP) as 273.15 K (0 °C) and 10^5 Pa (100 kPa, 1 bar, 0.99 atm).

1.10.5 Enthalpy

Another important consideration in thermodynamics is *enthalpy (H)*, the *heat content* of a system. In some cases enthalpy is expressed in units of calories (cal) or kilocalories (kcal), which makes sense because calories are a common measure of heat in everyday life; however, the SI units are joules (J) (or kilojoules, kJ).

Enthalpy is typically expressed as follows:

$$H = E + PV \tag{1.38}$$

or

$$dH = dE + PdV \tag{1.39}$$

But often the most important consideration related to enthalpy is the change in H ($\Delta H = H_2 - H_1$) during a reversible reaction, where the two values of H represent enthalpies associated with different states of matter, like liquid water and water vapor, or with elements in different bonding arrangements, e.g. Fe and O_2 vs. Fe_2O_3. ΔH is an important parameter in geochemistry because it expresses heat absorbed or released during changes of state (e.g. evaporation) or during chemical reactions that produce minerals, ions, or molecules. If heat is gained during a reaction (i.e. ΔH is positive), the reaction is endothermic; conversely, if heat is lost (ΔH is negative), the reaction is exothermic.

Given that reactions either consume or produce heat, we can calculate the difference in enthalpy between the reactants and products and determine the amount of heat produced (released) or consumed (absorbed) by the reaction. This is important because it is one of the ways that thermodynamics can help to predict the behavior of environmental systems such as soils and waters; typically, spontaneous processes produce (i.e. release) heat, i.e. spontaneous processes usually are exothermic (caveat: while this is generally true it is not always the case – for example, when some salts dissolve in water the solution gets colder. Dissolution of some salts absorbs heat from the water yet is a spontaneous process because the increase in entropy is more important than the positive ΔH).

Enthalpies of reactions ($\Delta H^o{}_R$) are determined by summing the *enthalpies of formation* ($\Delta H^o{}_f$) of all reactants and subtracting this term from the sum of $\Delta H^o{}_f$ values of all products (standard state conditions):

$$\Delta H^o{}_R = \Sigma\, n_x \times H^o f_x\ (\text{products}) - \Sigma\, n_x \times H^o f_x\ (\text{reactants}) \tag{1.40}$$

Enthalpies of formation are available from various sources and selected examples are presented in Appendix IV. By convention, $H^o f = 0$ for elements in their pure state (e.g. Fe, Si, Na) and for gases such as H_2, N_2, and O_2. In the $\Delta H^o{}_R$ reaction above, the $H^o f$ for each reactant or product (represented by the variable x) is multiplied by the number of moles (n) expressed in the reaction.

We can examine the reaction of Fe and O_2 to form hematite (Fe_2O_3) by the chemical reaction $2\,Fe + 1.5\,O_2 = Fe_2O_3$. Values of $H^o f$ (in kJ mol^{-1}):

$$H^o f\,(Fe) = 0$$

$$H^o f\,(O_2) = 0$$

$$H^o f\,(Fe_2O_3) = -824.2$$

It is crucial to remember to multiply $H^o f$ values by molar abundances presented in the chemical reaction.

$$\begin{aligned}\Delta H^o{}_R &= (1 \times -824.3) - (2 \times 0 + 1.5 \times 0)\\ &= -824.3\ \text{kJ mol}^{-1}.\end{aligned}$$

The negative $\Delta H^o{}_R$ for this reaction implies that it is spontaneous at standard ambient temperature and pressure, i.e. that iron will oxidize to form iron oxide.

Focus Box 1.25

Examples of Exothermic, Endothermic, Q, and H

Combustion of organic matter is clearly exothermic – we burn firewood and hydrocarbons to produce heat. Boiling of water, the transformation of andalusite to sillimanite during prograde metamorphism, and the maturation of petroleum in sedimentary basins are all endothermic processes – they absorb heat. The stored heat can then later be released; for example, stored heat in petroleum is released during the exothermic reaction known as combustion. It is worth pointing out the difference between two terms that represent heat, Q and H. Q represents flow of heat or heat transfer, for example from hot Hawaiian lava into cool ocean water; H represents heat stored within a system, such as the stored heat in petroleum, water vapor, or sillimanite.

Focus Box 1.26

Example of Enthalpy of Reaction

Under certain metamorphic conditions, calcite ($CaCO_3$) and quartz (SiO_2) react to form wollastonite ($CaSiO_3$) plus CO_2 according to this reaction:

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2 \tag{1.41}$$

Is this a spontaneous process at the earth's surface (i.e., 25 °C and 1 atm)? Values of H°f (in $kJ\,mol^{-1}$) are (Appendix IV):

$$H^o f\,(CaCO_3) = -1207.4$$

$$H^o f\,(SiO_2) = -910.7$$

$$H^o f\,(CaSiO_3) = -1630$$

$$H^o f\,(CO_2) = -393.5$$

The enthalpy of the reaction can then be determined as follows:

$$\Delta H^o_R = [(1\text{ mol} \times -1630\text{ kJ mol}^{-1}) + (1\text{ mol} \times -393.5\text{ kJ mol}^{-1})] - [(1\text{ mol} \times -1207.4\text{ kJ mol}^{-1}) + (1\text{ mol} \times -910.7\text{ kJ mol}^{-1})] = +94.6\text{ kJ}$$

This reaction requires addition of 94.6 kJ of heat (per mol of each reactant given the stoichiometry of the reaction), suggesting that it is not spontaneous (without considering entropy we cannot be sure – more on this in Section 1.10.6). Evidence from geology is consistent with this conclusion because calcite and quartz do not react to form wollastonite and carbon dioxide until systems reach medium-grade metamorphic temperatures and pressures (~500 °C, >1 kb).

1.10.6 Heat capacity

Heat capacity is the amount of heat required to raise the temperature of a given amount (1 mol or 1 g) of a substance by 1 °C. It is defined as the ratio of heat added relative to the extent of temperature increase, where the greater amount of heat required to cause an increase in temperature corresponds to higher heat capacity.

$$C = dq/dT \tag{1.42}$$

In this equation, C is heat capacity, and dq and dT are changes in heat and temperature. Rearranging emphasizes the point that, for a given amount of heat added (dq), the magnitude of temperature increase will be lower if the heat capacity (C) is high.

$$dT = dq/C \tag{1.43}$$

At constant volume, heat capacity can be expressed as:

$$C_v = (\delta q/\delta T)_v \tag{1.44}$$

Given Eq. (1.36), and realizing that $PdV = 0$ at constant volume, $\delta E = \delta q$ (at constant P), so δE can be substituted for δq:

$$C_v = (\delta E/\delta T)_v \tag{1.45}$$

Heat capacity at constant pressure (C_p) is defined as:

$$C_p = (\delta q/\delta T)_p \tag{1.46}$$

and Eq. (1.36) can be rearranged slightly to give:

$$dq = dE + PdV \tag{1.47}$$

Now, substituting the right side of Eq. (1.47) into the numerator of the right side of Eq. (1.46) gives:

$$C_p = (\delta E/\delta T)_p + P(\delta V/\delta T)_p \tag{1.48}$$

And given Eq. (1.39) (effectively, $\delta H = \delta E + P\delta V$),

$$C_p = (\delta H/\delta T)_p \tag{1.49}$$

Focus Box 1.27

Denoting "Change in" Using the Symbols d vs. Δ and δ in Equations

The symbols Δ, δ, and d are commonly used to signify change in quantity, e.g. dx/dy. From Eqs. (1.43) to (1.44), the notation shifted from d to δ. As used here, the symbol δ indicates that the derivation is performed with a restriction, in this case constant volume. The subscript v indicates that volume of the system is constant.

Focus Box 1.28

Examples of Heat Capacities of Substances

Comparing the heat capacity (at 25 °C) of liquid water (a relatively high value, C = 4.19 J/g·K) to dry rock (relatively low values in the range of 0.7 to 0.9 J/g·K) provides some insight into how heat capacity affects environment. The paucity of water in deserts means that rock is the dominant control on temperature change and this results in drastic temperature swings, both diurnally and seasonally. In moister regions such as tropical forests or temperate coastal regions, temperature extremes are minimized by the high heat capacity of water present in places such as lakes (or seas), air (as clouds or water vapor), vegetation, and soils. The high heat capacity of water allows it to function as a temperature buffer.

Heat capacity is an *extensive property*, i.e. it is dependent on the amount of the substance in question – the greater the amount of substance, the greater the amount of heat needed to be added to achieve the same change in temperature. That said, values of heat capacity are typically normalized to a mass of 1 g, meaning that effectively heat capacity is an *intensive property*, i.e. when normalized (divided by mass), it reflects a characteristic of a given substance independent of amount (i.e. mass).

1.10.7 Gibbs free energy and predicting stability

The *Gibbs free energy* (G) of a system accounts for changes in both enthalpy and entropy during reactions and is a useful tool in predicting stability – it considers change in enthalpy as well as change in entropy.

$$\Delta G^o{}_R = \Delta H^o{}_R - T\Delta S^o{}_R \quad (1.50)$$

Any reaction that produces a decrease in the Gibbs free energy is spontaneous – that is to say, any reaction for which $\Delta G^o{}_R$ is negative is spontaneous. Systems tend toward lower energy states in the absence of new addition of energy, so a decrease in G will produce a more *stable* system. In a schematic way (Figure 1.15), stability of a physical system can be used to illustrate this point. The ball at point A is unstable with respect to location, and to decrease this instability (high energy state), it will roll down to point B, and if it can overcome the slight energy barrier at point C, it will eventually achieve its most stable configuration by rolling down to point D.

Point B might be referred to as a *metastable* condition, one that is not the most stable configuration (that would be D), but one that may play a strong role in system behavior.

Determining Gibbs free energies for geochemical systems allows prediction of their behavior much like the

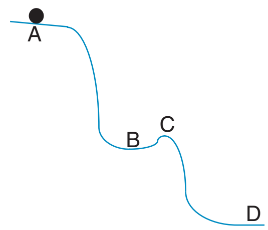

Fig. 1.15 Schematic diagram illustrating relative stability conditions, from unstable at points A and C, to metastable at point B and stable at point D. Note that the metastable point B can be reached from points A or C, and that to shift from metastable (B) to stable (D), some energy must be introduced. If not, the metastable condition may persist for a long time.

simple analysis of the ball between points A and D. For example, if magnetite (Fe_3O_4), water, and oxygen gas exist in a soil at standard conditions, we might ask, is this assemblage stable or of out of equilibrium? Is magnetite stable in this soil, or would we predict that it will eventually transform into an iron hydroxide such as goethite? The possibility that the system will react to form goethite (FeOOH) to achieve a lower energy state could be assessed according to this reaction:

$$2\,Fe_3O_4 + 0.5\,O_2 + 3\,H_2O = 6\,FeOOH \quad (1.51)$$

$\Delta G^o{}_R$ for the reaction is computed according to this equation:

$$\Delta G^o{}_R = \Sigma\, n_x \times G^o f_x\,(\text{products}) - \Sigma\, n_x \times G^o f_x\,(\text{reactants}) \quad (1.52)$$

Values for $G^o f$ (in kJ mol^{-1}) are (Appendix IV):

$$G^o f\,(Fe_3O_4) = -1015.5$$

$$G^o f\,(O_2) = 0$$

$$G^o f\,(H_2O_l) = -237.2$$

$$G^o f\,(FeOOH) = -488.6$$

Focus Box 1.29

Examples of "Metastability" in the Geochemical Realm

The mineral halloysite is a disordered form of kaolinite that forms in tropical soils when unstable igneous minerals such as olivine and pyroxene rapidly dissolve (over hundreds to thousands of years). Rapidly dissolution may lead to formation of metastable halloysite rather than kaolinite due to kinetic factors; once formed, halloysite may require hundreds of thousands of years to finally transform into thermodynamically stable kaolinite. Another example is aragonite ($CaCO_3$), which forms when marine organisms obtain dissolved calcium and bicarbonate from seawater to form shells. Aragonite is unstable relative to calcite but may persist for thousands of years or longer before increased temperature (e.g. burial in a sedimentary basin) or changing solution chemistry (e.g. in the pores of sediments) trigger the aragonite → calcite transformation.

These values produce the following equation:

$$\begin{aligned}\Delta G^o{}_R = {} & [6\ \text{mol} \times -488.6\ \text{kJ mol}^{-1}] \\ & - [(2\ \text{mol} \times -1015.5\ \text{kJ mol}^{-1}) \\ & + (0.5\ \text{mol} \times 0\ \text{kJ mol}^{-1}) \\ & + (3\ \text{mol} \times -237.2\ \text{kJ mol}^{-1})] = -189.0\ \text{kJ}\end{aligned}$$

What this negative Gibbs free energy value demonstrates is that magnetite is unstable in the presence of water and oxygen at the earth's surface and will react to produce goethite, a common soil mineral. What this reaction does not tell us is how fast this reaction will take place. Is there an energy barrier? Does the system need to overcome an activation energy like that at point C in the ball example of Figure 1.15? Does diffusion of O_2 or H_2O to magnetite surfaces limit reaction rate? In reality, magnetite can persist in soils in a metastable state for at least thousands of years, and that fact is not evident from this $\Delta G^o{}_R$ calculation. Section 1.11 on kinetics addresses some questions related to rates of processes.

1.10.8 The Van't Hoff equation: relating gibbs free energy to the equilibrium constant (K_{eq})

The Gibbs free energy of a reaction can also be expressed in terms of the equilibrium constant (K_{eq}), which is much like the K_a discussed earlier in this chapter when considering acids. Consider a general reaction at equilibrium where:

$$aA + bB = cC + dD \qquad (1.53)$$

A and B, and C and D are reactants and products, respectively, and the lowercase a, b, c, and d represent molar fractions of reactant or product. In this general case:

$$K_{eq} = [C]^c \times [D]^d / [A]^a \times [B]^b \qquad (1.54)$$

$[C]^c$ represents the concentration of reactant C raised to the c power, and so on. Products are in the numerator and reactants in the denominator. Or, for a more tangible example, we can write the K_{eq} for oxidation of ferrous iron (Fe^{2+}). The chemical reaction is:

$$4Fe^{2+} + O_2 + 10H_2O = 4Fe(OH)_3 + 8H^+ \qquad (1.55)$$

and:

$$K_{eq} = [Fe(OH)_3]^4 \times [H^+]^8 / ([Fe^{2+}]^4 \times [O_2] \times [H_2O]^{10}) \qquad (1.56)$$

However, by convention, the concentration of water is given the value of 1, and pure solid phases like ferrihydrite ($Fe(OH)_3$) are similarly assigned values of 1, so in this case the K_{eq} simplifies to:

$$K_{eq} = [H^+]^8 / ([Fe^{2+}]^4 \times [O_2]) \qquad (1.57)$$

which means that the main controls on the reaction are the concentrations of H^+ and Fe^{2+} and availability and reactivity (fugacity) of O_2. A high value for the K_{eq} indicates that the reaction will proceed in the direction of products. In other words, for reactions that favor products, the numerator will be greater than the denominator, producing a high K_{eq}. In cases where reactants are more favored (i.e. reactants are predicted to occur in higher concentrations than products), K_{eq} values are small.

Focus Box 1.30

Using the K_{eq} to Predict Reactivity

The dissolution of gibbsite in the presence of acidic soil water is represented by the following reaction,

$$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O \quad (1.58)$$

and the $K_{eq} = 10^{8.11}$ at 25 °C and 1 bar, which is often expressed in log form as log $K_{eq} = 8.11$ (Langmuir 1997). Expressed in K_{eq} form:

$$K_{eq} = [Al^{3+}]/[H^+]^3 = 10^{8.11} \quad (1.59)$$

The high value of the K_{eq} indicates that the system strongly favors dissolution of $Al(OH)_3$ and formation of dissolved Al^{3+}. (Of course, pH of the solution will strongly control the probability of this reaction.) Conversely, the dissolution of fluorite ($CaF_2 = Ca^{2+} + 2F^-$) has a log $K_{eq} = -10.6$ (i.e. a K_{eq} of $10^{-10.6}$), and this very low value indicates that fluorite is insoluble in water. The fact that the product of the concentrations of $[Ca^{2+}]$ and $[F^-]^2$ is extremely low ($K_{eq} = 10^{-10.6}$) indicates that the reactant side of the equation is favored, indicating that solid CaF_2 is the favored form of these components.

$\Delta G^o{}_R$ for a reaction is related to the K_{eq} and can be expressed as:

$$\Delta G^o{}_R = -RT\ln K_{eq} \quad (1.60)$$

This is the van 't Hoff equation, where R (the gas constant) is equal to 8.314 J mol^{-1} K^{-1} (8.314×10^{-3} kJ mol^{-1} K^{-1}) and T is temperature (in K), which produces units of J mol^{-1} (or kJ mol^{-1}) for $\Delta G^o{}_R$.

In most cases, Gibbs free energy data are determined for systems at 25 °C (298.15 K), so for systems at 25 °C (reasonably representative of surface environments), $\Delta G^o{}_R$ can be further simplified and converted to $\log_{10}$ as:

$$\Delta G^o{}_R = -5.708 \times \log(K_{eq}) \quad (1.61)$$

Typically enthalpy and entropy changes are not strongly temperature dependent, so given Eq. (1.50), the Gibbs free energy, ΔG, should vary in a linear manner with temperature. Rearranging Eq. (1.50) slightly and presenting the variables in a generic sense gives us:

$$\Delta G/T = \Delta H/T - \Delta S \quad (1.62)$$

By then substituting the right side of Eq. (1.60) for ΔG:

$$RT\ln K/T = -\Delta H/T + \Delta S \quad (1.63)$$

Then dividing and rearranging:

$$\ln K = -\Delta H/RT + \Delta S/R \quad (1.64)$$

Expressed in this way, Eq. (1.64) is an equation of a line: ln K = y, −ΔH/R is m (slope), 1/T is x and ΔS/R is b (constant). Two characteristic types of plots (Figure 1.16) result when different values for T are plugged in to Eq. (1.64).

Taking the derivative of Eq. (1.64) with respect to temperature gives a different formulation of the van 't Hoff equation:

$$d(\ln K)/dT = \Delta H/RT^2 \quad (1.65)$$

Note that the term ΔS/R disappears because both terms are constants (assuming S does not change with temperature).

Integrating Eq. (1.65) between temperatures T_1 and T_2 produces Eq. (1.66), another expression of the van 't Hoff equation, one which makes it possible, given a K value (e.g. K_1) at standard temperature (e.g. T_1), to determine an unknown value of K (e.g. K_2) at a different temperature (i.e. T_2).

$$\ln(K_2/K_1) = (-\Delta H/R) \times (1/T_2 - 1/T_1) \quad (1.66)$$

For calculations using this equation, R is the gas constant (8.314 J mol^{-1} K^{-1}) and temperature is in Kelvins. It is straightforward and can be useful.

1.11 KINETICS AND REACTION RATES

The thermodynamic approaches just presented are often insufficient to understand behaviors or states of ions and compounds in nature, especially in low-temperature systems like soils, waters, and the atmosphere. Determining rates of processes are addressed in the field of *kinetics*.

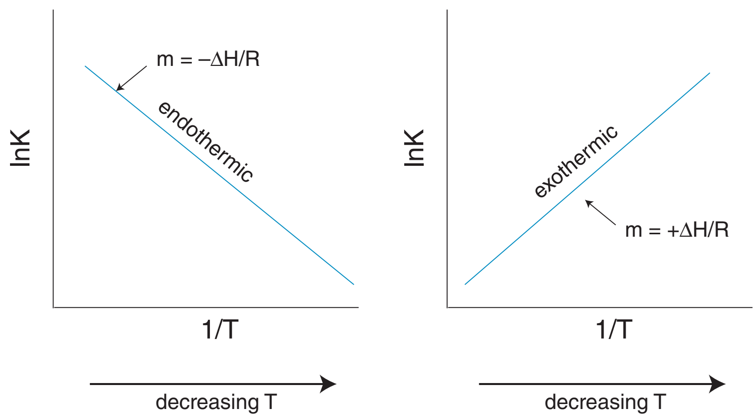

Fig. 1.16 Arrhenius plots showing relationship between equilibrium constant (K) and temperature for endothermic and exothermic reactions. For endothermic reactions, increasing temperature increases K, i.e. adding heat increases reaction rate; for exothermic reactions, the opposite is true.

Focus Box 1.31

Soils and Kinetics

Soils, for example, almost always contain minerals that are (i) thermodynamically unstable at the earth's surface, such as the olivine, augite, and plagioclase that form at $T > 800\,°C$ in cooling basalt lava, as well as (ii) minerals that are thermodynamically stable at low temperatures (25 °C, for example), such as calcite, kaolinite, and hematite. While the latter three can come to equilibrium with surface waters, olivine, augite, and plagioclase do not. Thermodynamics tells us that. What thermodynamics does not quantify is rate. Consider magnetite in tropical soils; thermodynamics (e.g. ΔG) indicates that it will transform to goethite, but it does not indicate how fast.

Reactions that occur slowly, are not reversible, or do not take place in a system at equilibrium for whatever reason (e.g. soils) are often best understood using kinetic approaches. The same can be said for *heterogeneous reactions*, those that involve various states of matter such as solid minerals and amorphous solids mixed with liquid and gas phases, conditions that tend to occur in soils, sediments, streams, aquifers, and the atmosphere.

1.11.1 Factors controlling reaction rate

Rates of reactions are controlled by numerous factors, including temperature, pressure, redox conditions, pH, mineral composition, abundance of organic matter, pore water composition, diffusion rates, bond types, biotic factors, system composition, and more. In many cases, reaction rates have been determined in laboratory studies that require extrapolation to natural environments and are often prone to large uncertainties (in some cases, an order of magnitude or more; refer to Section 9.1.2 and Table 9.1). The multitude of potential biotic factors can be harder to quantify than the main inorganic controls, yet it is important because biotic effects can be very influential. For example, plants can alter soil pH by exuding (releasing) H^+ from their roots into soil pores to enhance dissolution of nutrient-bearing minerals; another way that biological factors influence rates and stabilities is the oxidation and reduction reactions mediated by microbes. Thus, the complex array of variables influencing reaction rates can complicate kinetic analysis.

Biogeochemical processes are often controlled by a *rate-limiting step*, a step in a process that is much slower than others. Consider the *dissolution* of a mineral grain, a process that could involve five steps: (i) diffusion of reactant(s) toward the mineral surface (where a common example of a reactant is H^+); (ii) sorption of reactants onto the mineral surface; (iii) formation of a bond between the reactant and the part of the mineral grain under attack (perhaps the O atom bonded to a K^+ ion in a feldspar); (iv) desorption of the newly formed complex between reactant and mineral component (e.g. OH^-), and finally (v) transport of the newly formed product away from the mineral surface by diffusion. If any of one of the steps 1 through 5 is slower than others, it will be the rate-limiting step. In clay-rich sediments, diffusion (steps 1 or 5) can be a rate-limiting step, whereas in highly-insoluble minerals, step 3 (and/or 4) can be the rate-limiting step. Kinetic limitations on *crystal growth* are similar, and can be envisioned by reversing steps 1 through five.

1.11.2 Reaction rate, reaction order

Reaction rates are partly controlled by the order of the reaction, where reaction order is defined as the dependence of reaction rate on concentrations or ratios of species involved in reactions. Reactions can be of zero, first, second, or third order (first and second are most common in environmental geochemistry). Rates of zero-order reactions occur at rates independent of the concentration of the reactant(s); rates of first order reactions are controlled by the concentration of one reactant or product; rates of second-order reactions are controlled by concentrations of two reactants or products, or a reactant (or product) squared.

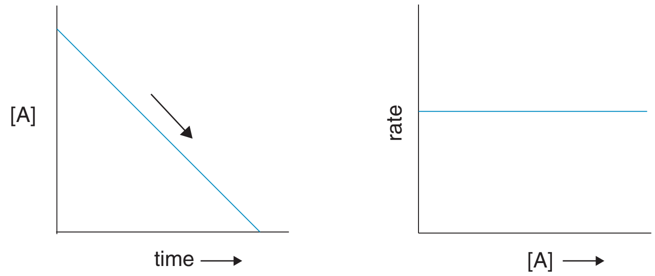

Fig. 1.17 Two graphical representations of zeroth (0th) order chemical reactions, where [A] represents concentration of a chemical species (e.g. ion, mineral, or compound). In the example on the left, decrease in concentration of A is linear, and on the right, rate of change is constant.

1.11.2.1 Zero-order reactions

In a *zero-order reaction*, rate is independent of the concentration of reactants. This reaction (sometimes called "zeroth-order" reaction) is one where reactant A undergoes transformation to product P, and can be represented by the simple chemical equation A → P. The following equation describes change in concentration of A (represented as [A]) with time (dt):

$$d[A]/dt = -k \quad (1.67)$$

The term k here is a constant, most likely determined by laboratory experiments or by studies of natural systems, and the negative sign indicates decreasing abundance of A with time. In integrated form, this equation is:

$$[A] = [A]_o - kt \quad (1.68)$$

$[A]_o$ represents the amount of A at time zero (where examples of t_o could be when sediments were deposited in a floodplain or when a gaseous compound was emitted into the atmosphere), and the negative sign for kt correlates to decreasing reactant with time. So the abundance of reactant A at any time, i.e. $[A]_t$ is merely determined by the amount of A at t_o, i.e. $[A]_o$, as well as how much time has passed (t), and the rate constant (k) that governs reaction of A into P. The rate of reaction is not controlled by the amount of A. Plotted graphically (Figure 1.17), it becomes clear that, for 0th order processes, [A] decreases in a linear fashion with time, and rate does not vary with time.

1.11.2.2 First-order reactions

A *first-order reaction* is one where rate depends on the concentration of a reactant (or product) raised to the first power – that is, first-order reactions are typically proportional to the concentration of a reactant, a good example being radioactive decay. The equation for a first-order reaction representing decreasing A with time is:

$$d[A]/dt = -kA \quad (1.69)$$

Literally, the rate of decrease of A depends on the rate constant (k) multiplied by the amount of A present at time t. In its integrated form, this equation is:

$$[A] = [A]_o \times e^{-kt} \quad (1.70)$$

Focus Box 1.32

Examples of Zero-Order Reactions

In nature, zero-order reactions are uncommon, because for most reactions, rate increases as the probability of interactions among reactants increases; stated in another way, reaction rate usually increases with increasing concentration of reactants, at least in part because more reactant means more likelihood of interacting with other reactants to foster the reaction (this concept is covered in first- and second-order reaction kinetics). Nonetheless, dissolution of salts like halite ($NaCl \rightarrow Na^+ + Cl^-$) and fluorite ($CaF_2 \rightarrow Ca^{2+} + 2F^-$) in dilute solutions has been described as zero-order, or pseudo-zero-order (Posey-Dowty et al. 1986). The "pseudo-zero-order" qualifies the observation that rate is slightly nonlinear compared to the idealized plots in Figure 1.17.

Focus Box 1.33

Example of a First-Order Reaction

In the case of radioactive decay, the amount of daughter isotope (e.g. ^{222}Rn produced by decay of ^{226}Ra) produced per unit time decreases as the amount of parent isotope (e.g. ^{226}Ra) decreases; in other words, as reactant is used up during the reaction, the rate of formation of products decreases (which is not to say that the amount of product decreases – it continues to increase, but at a progressively slower rate). In Figure 1.18, [A] decreases exponentially (and the product increases parabolically, following the dashed line) while the rate of change is controlled by the amount of A (reactant) – less A equals lower rate. In Figure 1.18, the solid line would represent amount of parent isotope (and the dashed line amount of daughter isotope) in a radioactive decay reaction.

Graphically, first-order reactions depict nonlinear changes in concentration with time as well as rates that vary as a function of the concentration of reactants (Figure 1.18) – note that the rate (expressed as, e.g., mol yr^{-1}) varies but the rate constant (expressed as a percent or proportion, does not).

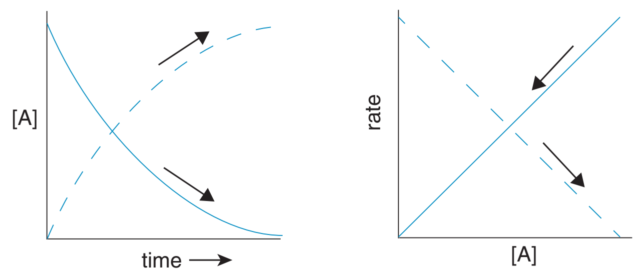

Fig. 1.18 Two graphical representations of first (1st) order chemical reactions, where [A] represents concentration of a chemical species. On the left, change in concentration of A is logarithmic (solid line) or exponential (dashed line); on the right, for both cases (increasing or decreasing concentration), rate of change decreases in a linear fashion with time. Arrows in diagrams indicate direction of forward reaction (emphasizing that, on the right, the solid line represents decreasing [A] with time).

1.11.2.3 Second-order reactions

Rates of *second-order reactions* are proportional to the concentration of a reactant squared (dependent on A where $2A \rightarrow B$), or in some cases to the product of the molar concentrations of two reactants (where $A + B \rightarrow C$).

$$d[A]/dt = -kA^2 \textit{ or } d[A]/dt = -kAB \quad (1.71)$$

and integrated, the first equation can be expressed as:

$$1/[A] = k \times t + C \quad (1.72)$$

And given that $[A] = [A_o]$ when $t = 0$,

$$1/[A] - 1/[A_o] = k \times t \quad (1.73)$$

When depicted graphically (Figure 1.19), second-order reactions exhibit rapid initial changes in concentrations and progressively slower rates with time, and rate increases exponentially with higher concentrations of reactant(s).

Kinetics and reaction order can be summarized with this equation:

$$2A + B = A_2B \quad (1.75)$$

Focus Box 1.34

Examples of Second-Order Reactions

The reaction of nitrogen dioxide to nitrogen monoxide plus oxygen – one that plays an important role in atmospheric chemistry – is modeled as a second-order reaction:

$$2NO_2 = 2NO + O_2 \quad (1.74)$$

In this case, rate is dependent on abundance of NO_2, and given that the concentration of the reactant NO_2 is squared (Eq. (1.71)), that rate will be high initially but will decay rapidly as shown in Figure 1.19. Another example of a second-order reaction is the desorption and leaching of soluble cations (e.g. K^+, Ca^{2+}) from tropical soils over time. Rate is initially very high but then decays rapidly as abundance of the reactants decreases (Fisher and Ryan, 2006). Ion exchange of heavy metals also has been modeled as second-order kinetics (Lee et al. 2007; Zewail and Yousef 2015).

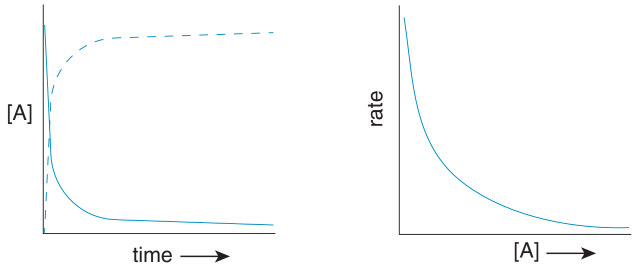

Fig. 1.19 Two graphical representations of second (2nd) order chemical reactions, where [A] represents concentration of a chemical species. In the example on the left, [A] decreases exponentially, and on the right, we see that rate of change decreases exponentially with time.

If the reaction rate depends on the concentration of none of the components in Eq. (1.75), then it is a zero-order reaction. If rate depends on the concentration of B in Eq. (1.75), then it is first-order, and if it depends on the concentration of A, it is second-order. If it depends on the concentration of A, B, and the product A_2B, it is third-order (and first order with respect to B and A_2B, and second order with respect to A), but this is a rare occurrence in geochemical systems.

1.11.3 Temperature and the Arrhenius equation

Temperature also plays an important role in reaction rate – higher temperatures usually foster higher reaction rates. In biogeochemical systems, reaction rates tend to double, triple, or quadruple for every increase of 10 °C. The greater energy imparted by higher temperature tends to enhance interactions between reactants, thus enhancing the probability of productive interactions (and here we must be referring to first- and second-order reactions). Higher temperature can also overcome *activation energies* that can sometimes serve as barriers like the one depicted schematically in Figure 1.15. The Arrhenius equation relates temperature to the rate constant:

$$k = A \times e^{-E_a/RT} \tag{1.76}$$

where E_a is activation energy, R is the gas constant, T is temperature (K), and A is the temperature-independent term known as the pre-exponential factor or the A factor – it serves to convert the product term into values appropriate for k of different reaction orders. In a qualitative sense, and because *e* is raised to the *negative* E_a/RT, increasing temperature will increase k, speeding up the reaction. Plots of the effect of temperature on reaction

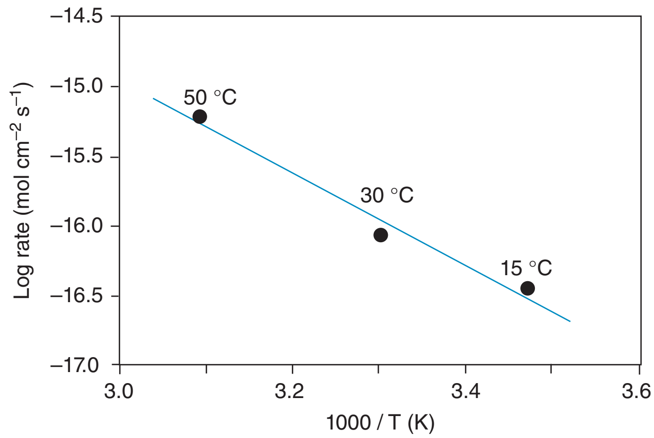

Fig. 1.20 Effect of temperature on chemical weathering rate of rhyolite as a function of temperature. Source: Adopted from Yokoyama and Banfield 2002.

rate are typically plotted as inverse of T (1/T, where T is in Kelvins) versus log of the rate constant k, a type of graph known as an Arrhenius plot. Figure 1.20 depicts dissolution rate of powdered rhyolite (compositionally similar to granite; Table 1.1) as a function of temperature.

The rates shown in Figure 1.20 increase more than 10-fold with a temperature increase of approximately 35 °C (note log scale of y-axis).

This introduction to equilibrium thermodynamics and kinetic constraints is designed to present some of the concepts, approaches, and limitations contained within these two important fields. In the following chapters some of these approaches are applied to predicting and understanding behaviors of environmental systems. For more detailed treatments of this topic, the reader is referred to excellent and much more thorough treatments of these topics in geochemistry texts by James Drever (*The Geochemistry of Natural Waters*), Gunter Faure (*Principles of Geochemistry*), and Donald Langmuir (*Aqueous Environmental Geochemistry*). The *Kinetics of Geochemical Processes* issue of *Reviews in Mineralogy* edited by Lasaga and Kirkpatrick (1981) also presents various perspectives on this topic.

QUESTIONS

1.1 Magnetite, hematite, and goethite all occur in tropical soils. Rank them in order of thermodynamic stability in oxidized soil at 25 °C. Which is more likely to be released into soil water, a trace element (e.g. arsenic) substituted into the structure of hematite or goethite? Explain.

1.2 What is (are) the oxidation state(s) of manganese in each of the following compounds?

MnO_2 Mn_3O_4 MnO $MnCO_3$

1.3 Recalculate the chemical compositions of the igneous rocks given below, one mafic (#1) and one felsic (#2). First determine weight percent concentrations as elements (i.e. convert the oxide values to elemental values) and rank them in terms of their abundance. Also calculate concentrations of each element in terms of mg kg^{-1} and mol kg^{-1}. Using a spreadsheet would be a time-effective way to do this problem compared to using a calculator.

	#1	#2
SiO_2	45.0	68.0
Al_2O_3	3.5	15.0
FeO	8.0	3.2
Fe_2O_3	0.0	1.3
MgO	39.0	1.7
CaO	3.2	3.4
Na_2O	0.32	3.1
K_2O	0.04	3.6
Cr_2O_3	0.42	1.1×10^{-3}
NiO	0.25	9.2×10^{-4}

1.4 Why are elements with even atomic numbers more abundant than their neighbors with odd atomic numbers? Explain with appropriate nuclear reactions.

1.5 Why is Fe more abundant than neighbors with similar atomic #? Describe with appropriate nuclear reactions.

1.6 Why is Pb more abundant than neighbors with similar atomic #? Describe with appropriate nuclear reactions.

1.7 List the units of concentration that are commonly used in the following cases (consider mass-based and molar units):

A. Acids in water.
B. Salts in water.
C. Metals in soil.
D. Metals in water.
E. SiO_2 in rock.

1.8 Do the following calculations related to concentrations of solutions:

What is the concentration of Ca^{2+} (in ppm, i.e. mg l^{-1}) in a 4.7×10^{-5} M solution of $CaCl_2$? What is the concentration of $CaCl_2$ (in ppm) in the same solution?

You need to prepare 100 mL of a 10.0 mg l^{-1} solution of NO_3^- from KNO_3 powder. How much KNO_3 do you need to add? What would be the resulting concentration of K^+ (in mol l^{-1} and mg l^{-1})?

1.9 **A.** Write the chemical reaction for the dissolution of barite.
B. Calculate the change in enthalpy associated with the dissolution of $BaSO_4$ (barite).
C. Based on your result, predict how the solubility of barite varies with temperature.
D. Calculate the Gibbs free energy for the dissolution of barite into ions.
E. Calculate the solubility of barite at 25 °C and 1 atm.
F. Given that Ra coprecipitates with Ba, predict the solubility of Ra in groundwaters (a) ~lacking Ba (e.g. 1 ppb); and (b) rich in Ba (e.g. 100 ppb).

1.10 Which compound is more soluble in water, MgO, or CaO? Explain your reasoning.

1.11 Examine the kinetics of dissolution of a salt like NaCl by experimentation using an approach like that described by Velbel (2004).

1.12 Balance the following chemical reactions:

$$C_3H_8 + O_2 = H_2O + CO_2$$

$$CaCO_3 + H_2SO_4 = Ca^{2+} + SO_4^{2-} + H_2O + CO_2$$

$$Al(OH)_3 + H_4SiO_4 = Al_2Si_2O_5(OH)_4 + H_2O$$

$$CaAl_2Si_2O_8 = Ca_3Al_2Si_3O_{12} + Al_2SiO_5 + SiO_2$$

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