

Chapter 13: Water and the Lithosphere

Preview

The chemistry of water has a profound effect on our planet. Because of liquid water, Earth has a very different character than its neighbors in the solar system. In this chapter, we consider how water interacts with Earth's solid matter, the lithosphere. Topics include

- The acid-base properties of the planet
- The critical role of carbonate in the carbon cycle
- Weathering and solubility equilibria
- Ion exchange
- Effects of acidification on water and land

13.1 The Earth as Acid-Base Reactor

The earth is believed to have formed some 4.5 billion years ago from the coalescence of meteorites that circled the early sun. Heating from gravitational forces and nuclear decay melted the interior of the evolving planet, allowing the minerals to separate according to their density. The result is a molten core, mainly of iron, and a surrounding mantle, formed mainly of silicate-based rock, silicon and oxygen being by far the most abundant elements in the mantle. The heating of the earth led to plate tectonics, the thermally-induced circulation of segments of the mantle, which leads to the spreading of crustal plates at mid-ocean ridges, and subduction and uplift of crustal material at the plate boundaries, which are found at continental margins.

Volatile compounds, such as H_2O , HCl , CO_2 , SO_2 and N_2 were expelled from the interior in volcanic eruptions, forming the oceans and the atmosphere. This natural separation of volatile and non-volatile compounds was also a separation into acidic and basic compartments, because CO_2 , SO_2 and especially HCl are acidic, while the minerals left behind tend to be basic. The basicity of the lithosphere arises principally from the alkali metals and alkaline earths, especially Na, K, Mg and Ca, which are relatively common in the earth's crust (**Table 13.1**). These elements form basic oxides, which are incorporated into the dominant silicate framework of the major mineral phases. In addition, calcium carbonate (sometimes containing magnesium as well), or *limestone*, is abundant in the earth's crust, and carbonate is a basic anion [see p?].

The fundamental reason for this global acid-base separation is that the base-forming elements at the left side of the periodic table form exclusively ionic bonds, because of their relatively low nuclear charge; consequently their compounds are non-volatile ionic solids. However, the acid forming elements toward the right of the periodic table have a stronger tendency to form covalent bonds, because of their higher nuclear charge, and more readily produce isolated [volatile] molecules.

The earth's volatile acids react back with the non-volatile bases through the aqueous medium of the hydrosphere. Thus the seas are salty because the outgassed HCl dissolved in the condensed H_2O and reacted with the most basic constituents of the earth's crust, mainly the sodium oxide equivalents in silicate minerals, in a gigantic neutralization reaction. Although this happened a long time ago, global neutralization continues to this day in the form of rock *weathering*. The earth's tectonic processes

expose new crustal material to the atmosphere, where rainfall mediates erosion of the rock through neutralization reactions.

The principal acidic constituent of today's atmosphere is CO₂. It dissolves limestone by neutralizing the carbonate ions:

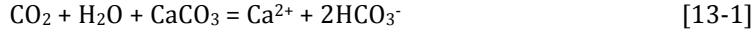


Table 13.1 Major Elements in Earth's Crust and Their Abundance in Seawater

Element	Crustal average (percent)	Seawater (ppm)
O	46.6	(88%)
Si	27.7	3
Al	8.1	1 x 10 ⁻³
Fe	5.0	3 x 10 ⁻³
Ca	3.6	0.041
Mg	2.1	1.3 x 10 ³
Na	2.8	1 x 10 ⁴
K	2.4	3.9 x 10 ⁻²
Ti	0.44	1 x 10 ⁻³
H	0.14	(10%)
P	0.11	0.09
Mn	0.10	2 x 10 ⁻³
F	0.06	1.3
Cl	0.01	1.9 x 10 ⁴
Ba	0.04	0.02
Sr	0.04	8
S	0.03	0.09
C	0.02	28
Mo	0.0003	1 x 10 ⁻⁴

The acid-base reactions of silicate rocks are harder to capture in chemical equations because of the complexity of silicate chemistry. Silicon dioxide, or *silica*, is a polymeric solid with a three-dimensional network of silicon atoms bound in a tetrahedral structure to four oxygen atoms, each of which are bound in turn to two silicon atoms (**Figure 13.1**). In silicate minerals, this network is rearranged to accommodate other metal oxides. When these oxides are neutralized through weathering, the network rearranges further, to produce a *secondary* mineral. For example, weathering of the mineral *feldspar*, NaAlSi₃O₈, can be represented as:

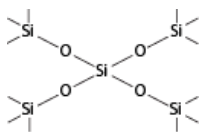


Figure 13.1 Polymeric structure of silicon dioxide.

$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ is the formula for the secondary mineral *kaolinite*, a member of the clay mineral class. Although it has a specific structure [see p. ?], it can formally be considered as being made up of a mole of Al_2O_3 , two moles of SiO_2 , and two moles of H_2O . Likewise, a mole of feldspar can be considered as a mole of Al_2O_3 three moles of SiO_2 and one mole of Na_2O . The acid-base part of the reaction involves the neutralization of Na_2O by H_2CO_3 to form two moles of sodium bicarbonate. But when this happens, the feldspar is converted to kaolinite, with the release of two moles of SiO_2 in the hydrated form, $\text{Si}(\text{OH})_4$. This form, *silicic acid*, exists as free molecules in very dilute solutions. As rain falls on feldspar, the sodium bicarbonate and silicic acid gradually leach away, leaving kaolinite behind. This is a very slow process, but the accumulation of kaolinite, and of other clays from other silicate minerals, is a key to the formation of soils.

The weathering of limestone [reaction [13-1]] is much faster than the weathering of silicate minerals, since no rearrangement of the crystal lattice is required. Both types of weathering are greatly accelerated if the rain contains strong acids, such as sulfuric or nitric acids. In this case protons work directly on the minerals, instead of through the weakly acidic H_2CO_3 molecules. This is why statues and stone buildings erode rapidly when exposed to acid pollution.

13.2 Organic and Inorganic Carbon Cycles

In parts II and III, we discussed the carbon cycle [pages xx] which results from the biological processes of photosynthesis and respiration, and the disturbance of this cycle by the burning of fossil fuels. In reality, the cycle of photosynthesis and respiration is imbedded in a much more complex biogeochemical cycle, involving sedimentation and burial, and the tectonic processes of the earth's crust.

This larger cycle (**Figure 13.2**) is actually two cycles, linked by the CO_2 molecule. One cycle is organic, and involves the photosynthesis/respiration and combustion balance, and also the burial of reduced carbon compounds, together with their reoxidation when the rock bearing them is exposed to the atmosphere through geological uplift. The other cycle is inorganic, and involves the weathering of silicate rocks, the precipitation of calcium carbonate in the ocean, and finally the conversion of the carbonate to calcium silicates plus CO_2 through tectonic activity. The geological phases of these cycles operate very slowly, on time scales of millions of years, but they ultimately control the level of CO_2 in the atmosphere.

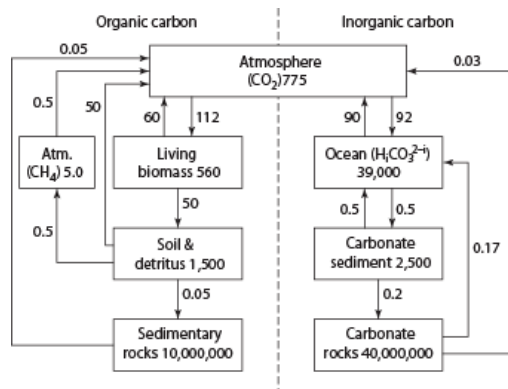


Figure 13.2 Reservoirs (boxes) and annual flows (arrows) of carbon (in units of 10^{15} g) through the organic (left) and inorganic (right) cycles. Outputs from the atmosphere to living biomass and the ocean are roughly 2×10^{15} g larger than inputs to the atmosphere from the living biomass and the ocean. This is attributed to net accumulation of carbon in these reservoirs owing to anthropogenic emissions of CO_2 from the burning of fossil fuels (see Figure 3.14 and ensuing discussion, p. ?).

13.2a The carbonate control

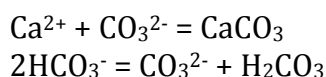
The chemistry of the organic carbon cycle was laid out in Part III. Green plants harness solar photons and store chemical energy by reducing CO_2 to carbohydrates via photosynthesis:



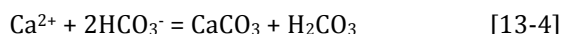
Energy is released through the reverse reaction, during respiration or combustion. The annual exchange of carbon between the living biosphere and the atmosphere is large, 110×10^{15} g (**Figure 13.2**), amounting to flows that are about one-fifth and one-seventh of their respective reservoirs. [The regular seasonal variations in this flow can be seen in the saw-tooth pattern of the atmospheric CO_2 record (**Figure 3.12**)]. About half of the return flow of C to the atmosphere goes by way of decomposition of soils and marine sediments, a reservoir of reduced carbon that is nearly three times the size of the living biosphere. [A small part of this latter flow occurs by way of methane release to the atmosphere and subsequent oxidation to CO_2 .] A tiny fraction of the reduced carbon, 0.05×10^{15} g/yr, is buried in sedimentary rock, and is eventually oxidized back to CO_2 when the rock is recycled in the crust and exposed to the atmosphere. Although the rate of burial is low, the amount of reduced C accumulated in rock over the eons is enormous, 10^{22} g; the turnover time is 200 million years. It is this part of the cycle that we are accelerating by burning fossil fuels. Even though fossil fuel deposits account for less than 1% of buried reduced carbon (**Figure 7.1**, p. ?), the rate of oxidation is so much faster than the natural rate, that the CO_2 reservoir size is being significantly increased.

The chemistry of the inorganic carbon cycle is determined by the solubility of calcium carbonate. The pH of the ocean is about 8, reflecting the basic character of the minerals with which it is in contact. CO_2 dissolves readily at this pH, the carbonic acid being converted to bicarbonate. The ocean is therefore a vast store of inorganic carbon ($39,000 \times 10^{15}$ g; **Figure 13.2**).

A small fraction of this carbon is present as CO_3^{2-} . [Since the pK_a of HCO_3^- is 10.33, the $[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$ ratio at pH 8 is $10^{-2.33}$ or 0.005]. However its concentration is sufficient that when Ca^{2+} enters the ocean as a result of the weathering of terrestrial rocks, calcium carbonate precipitates [mostly as shells of sea creatures]. As a result more carbonate is formed via the disproportionation of bicarbonate ion:

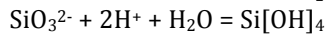


The overall process is:



The precipitation of each mole of calcium carbonate produces a mole of H_2CO_3 , thereby adding CO_2 to the atmospheric reservoir. However, if the source of the calcium [or magnesium] is weathering of terrestrial carbonate mineral, then reaction [13-4] has been run in reverse on land, and the net effect on global CO_2 is zero. Weathering of terrestrial carbonates consumes the same amount of CO_2 as is released by precipitation of carbonates in the ocean.

The situation is quite different when silicate minerals are weathered, because, silicate acts as a base but contributes no bicarbonate to the pool. Silicate weathering reactions are complex [see e.g. the feldspar weathering reaction, [13-4]], but the essence of the acid/base process is that the equivalent of one SiO_3^{2-} unit consumes two protons and is converted to $\text{Si}[\text{OH}]_4$:



If the protons are provided by CO_2 , and if the silicate is the source of the Ca^{2+} ions that later precipitate carbonate in the ocean, then the silicate weathering contribution to the carbon cycle can be represented as



When this reaction is added to the carbonate precipitation reaction [13-4], the resultant is



Thus if silicate, rather than carbonate, is the source of the Ca^{2+} that subsequently produces carbonate precipitation, then one mole of H_2CO_3 [or equivalently of CO_2] is consumed for every mole of carbonate precipitated. Consequently, silicate weathering draws down the atmospheric reservoir of CO_2 .

In fact weathering provides negative feedback on fluctuations in the CO_2 level, because of the operation of the greenhouse effect. The weathering rate increases with temperature and with moisture. If the CO_2 rises, so does the earth's surface temperature and the flow of water through the geological cycle. The weathering rate increases, and so does the flow of CO_2 to the carbonate sediments, thereby diminishing the atmospheric CO_2 concentration. This mechanism acts to stabilize CO_2 levels over geologic time.

If reaction [13-6] operated only in the forward direction, then CO_2 would slowly but surely disappear from the atmosphere. However, the reaction is eventually reversed by the operation of plate tectonics. As the earth's crust is subducted at the plate boundaries, the increase in temperature and pressure reverses reaction [13-6]; the volatile components, H_2O and CO_2 , escape through volcanoes, leaving the silicate rock behind. This process completes the inorganic carbon cycle.

As seen in Figure 13.2, most of the earth's carbon is trapped in carbonate rock. This reservoir is 40×10^{15} g, four times larger than the reduced carbon reservoir in rocks. The rate of carbonate rock formation from sediment is 0.2×10^{15} g/yr, but most of this flow is reversed by redissolution of carbonate in the ocean. [Calcium carbonate dissolves in the deep ocean because of increasing levels of CO_2 which result from the decomposition of organic matter as it sinks toward the bottom, and from the increase in CO_2 solubility at low temperatures and high pressures.] The rate at which the carbonate

rock is recycled to silicate and CO₂ through tectonic activity is only 0.03 x 10¹⁵ g/yr. Dividing this into the carbonate rock reservoir gives a residence time of 1.3 billion years. Thus the inorganic carbon cycle operates over a very long time indeed.

13.2b Carbonate sequestration

One of the ideas for sequestering the CO₂ currently emitted to the atmosphere by burning fossil fuels is to react the CO₂ with basic minerals (see Chapter 7, p ?); this idea amounts to speeding up the weathering process. If limestone were used as the reactant [reaction [13-1], soluble bicarbonate would be the product, and would require long-term disposal as a liquid, possibly in the deep ocean. However if calcium or magnesium silicates are used as the reactant, then the product would be insoluble CaCO₃ or MgCO₃ [reaction 13-6], which could simply be buried in the ground.

Calcium and magnesium silicates are abundant in the earth's crust, and concentrated deposits of magnesium silicates are common, especially near the continental margins, where people are also concentrated. It would be technically feasible to collect CO₂ from power plants, or from reforming plants where fossil fuels are converted to H₂ and CO₂, and ship it to magnesium silicate mines. Here the CO₂ could be reacted with the silicate, and the resulting MgCO₃ and silica could be deposited back in the mine. The main problem is the slowness of mineral phase reactions. They can be speeded up by grinding the mineral [to increase surface area] and by elevating the pressure and temperature. Additional rate enhancement could be obtained by using a secondary volatile reactant that is a stronger acid than CO₂ [e.g. HCl]; the secondary acid could be recovered in a separate heating step. However, the additional reaction loop would add complexity and a corrosive chemical to the process.

Even if the reaction rate problem can be overcome, it is not clear whether mineral carbonation is superior to direct injection of CO₂ into the oceans or into deep aquifers [p. ?]. Solid carbonates offer the advantage of thermodynamic stability, whereas injected gases could leak out over time [the leakage rate is a major issue to be evaluated in various injection schemes]. However, the costs of mineral carbonation may be higher than direct CO₂ injection, and public reaction to the required mining operations may be problematic.

13.2c CO₂, H₂O and Earth's planetary neighbors

The inorganic carbon cycle is an instructive vantage from which to compare Earth's atmosphere with the very different atmospheres of its neighboring planets, Venus and Mars. Venus has a runaway greenhouse effect, as a result of a massive atmosphere [100 times Earth's atmospheric mass] which is 98% CO₂. Venus is closer to the sun and has twice as high a solar flux, but dense clouds reflect 75% of the sunlight, producing a radiative temperature, 229 K, which is actually lower than that of Earth [255 K –see p. ?]. However the greenhouse effect raises the surface temperature to 750 K. There is no liquid water, and water vapor amounts to only 0.1% [by weight]. It is likely that the surface of Venus was never cool enough to allow water to liquify, and that most of the water outgassed from the planet's interior was eventually lost via ultraviolet photolysis and loss of the hydrogen to outer space. Without water there was no trapping of the CO₂ as carbonate, and the outgassed CO₂ stayed in the atmosphere.

In contrast to Venus, Mars is much colder than Earth. The solar flux is less than half that of Earth, and the radiative temperature is only 210 K. Moreover there is little greenhouse warming [8 K], because although, like Venus, the atmosphere is mostly

[95%] CO₂, it is very thin, less than 0.01 % as massive as that of Venus. Part of Mars' CO₂ and essentially all of its water is locked in its ice-caps. However, the Martian terrain bears clear evidence of liquid water in the past. Evidently Mars was tectonically active, and outgassed its volatile compounds, just as earth did, but that tectonic activity ceased, perhaps a billion years ago. With a diameter only half that of Earth, Mars would have lost internal heat much faster; internal heat is the driving force for the circulation of the planet's crust. Without tectonic activity, outgassing would have stopped, and weathering would have drawn down the atmospheric CO₂, and its greenhouse warming, until surface temperatures no longer permitted water to remain liquid. Thus Earth had two key advantages over its neighbors: a sufficient distance from the sun to permit water to remain liquid at the surface, and sufficient size and internal heat to maintain tectonic activity. These attributes produced a planet that is neither too hot nor too cold [this has been called the 'Goldilocks effect'], but just right for the evolution and maintenance of life.

13S.1 Weathering and Solubilization Mechanisms

13S.1a Ionic solids and the solubility product

Although water is generally an excellent solvent for ions, many ionic compounds are only sparingly soluble because the ion-water forces are outweighed by the forces that hold the ions together, particularly when the ions can arrange themselves in an energetically favorable way in a crystalline lattice. The energies stabilizing a lattice are generally maximal when the positive and negative ions have equal size and/or charge. For example, lithium fluoride is less soluble than lithium iodide because fluoride is closer in size to the small lithium ion than is iodide; in contrast, cesium iodide is less soluble than cesium fluoride because the cesium ion is closer in size to iodide. Similarly, both sodium carbonate and calcium nitrate are highly soluble because the positive and negative ions differ in charge, but calcium carbonate is sparingly soluble because both the cation and anion are doubly charged and therefore have a large lattice energy. Magnesium carbonate is more soluble than calcium carbonate, while sodium silicates are more soluble than potassium silicates, in both cases because the smaller cations fit the lattice less well, and interact more strongly with water. These differing solubilities account for magnesium and sodium being much more abundant in seawater, than calcium and sodium, respectively, despite the similar abundance of these pairs of metals in the earth's crust (**Table 13.1**).

The solubility of a sparingly soluble salt is governed by the equilibrium constant for the dissolution reaction, called the solubility product, K_{sp} . For example, barium sulfate dissolves with a solubility product K_{sp} of 10^{-10} :



$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 10^{-10} \text{ M}^2 \quad [13-7]$$

[BaSO₄ does not appear in the equation because the effective concentration of a solid phase is constant.] Equation (13-7) is valid as long as there is solid barium sulfate in equilibrium with the solution. If the concentration product of Ba²⁺ and

SO₄²⁻ exceeds the value of K_{sp}, barium sulfate will precipitate. It actually does precipitate on dead phytoplankton in the ocean, because their decomposition produces enough sulfate that the barium ions in the ocean are sufficient to exceed the solubility product.

Worked Problem 13.1: BaSO₄ Solubility

Q: What is the solubility of barium sulfate in a) pure water, or b) one millimolar sodium sulfate?

A: a) When pure water is equilibrated with barium sulfate, the concentration of barium matches the concentration of sulfate in solution:

$$[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = K_{\text{sp}}^{1/2} = 10^{-5} \text{ M}$$

Thus the BaSO₄ solubility is 10⁻⁵ M.

b) When either Ba²⁺ or SO₄²⁻ is present in excess, the solubility is the concentration of its partner, which decreases in inverse proportion to the excess concentration, via equation [13-7]. Thus when [SO₄²⁻] = 1 x 10⁻³ M, the solubility is [Ba²⁺] = K_{sp}/[SO₄²⁻] = 10⁻¹⁰ M²/10⁻³ M = 10⁻⁷ M.

13S.1b Solubility and basicity

If one of the ions of a sparingly soluble salt is an acid or a base, then the solubility increases, because the ion is partially converted to its basic or acid form, thereby pulling the solubility equilibrium toward more dissolution. For example, the K_{sp} of calcium carbonate is 10^{-8.24}, and if the only reaction were



the solubility would be 10^{-4.17}. However, the solubility equilibrium is shifted to the right because the basic carbonate ion reacts further with water [p. ?]



and is largely converted to bicarbonate .

The solubility is increased further when the solution is exposed to the atmosphere, because the carbonate ion then reacts with the acidic CO₂



The equilibrium constant is large, so the equilibrium lies far to right, and the CaCO₃ solubility is increased considerably. [Reaction 13-10 is obtained by subtracting the two successive dissociation reactions of H₂CO₃ [p. ?], so the equilibrium constant is obtained by dividing the two acidity constants.]

Worked Problem 13.2: Calculating the CaCO₃ Solubility

The combination of solubility and acid-base equilibria can make for fairly complicated calculations, and it is important to keep one's eye on the main reactions going on. Their *stoichiometry* [the number of reactants and products consumed and produced] provide the key equalities.

In the case of calcium carbonate in contact with water [but not with the atmosphere], there are two reactions to consider



To obtain the equilibrium constant for the second reaction, [which we will label K_4] we recognize that the equation is obtained by adding equations [13-8] and [13-9], so

$$K_4 = K_{sp}K_b = 10^{-12.01} = [\text{Ca}^{2+}][\text{HCO}_3^-][\text{OH}^-]$$

If [13-8] is the main reaction, then $[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] = K_{sp}^{1/2} = 10^{-4.17}$, or 0.67×10^{-4} M. On the other hand, if [13-11] is the main reaction, then its stoichiometry requires that the concentrations of all three product ions be the same: $[\text{Ca}^{2+}] = [\text{HCO}_3^-] = [\text{OH}^-]$. Consequently $[\text{Ca}^{2+}]^3 = K_4$, giving $[\text{Ca}^{2+}] = 10^{-4.00}$ M, which is about 50% higher than the value, obtained by considering reaction [13-8] alone.

To take both reactions into account we recognize that the total Ca^{2+} concentration must be the sum of the concentrations of carbonate and bicarbonate:

$$[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] \quad [13-12]$$

[This is an example of a *mass balance*]. But also, from reaction [13-11], $[\text{HCO}_3^-] = [\text{OH}^-]$. Substituting this equality into the equilibrium expression for reaction [13-11], allows us to express $[\text{HCO}_3^-]$ in terms of $[\text{Ca}^{2+}]$:

$$[\text{HCO}_3^-]^2 = K_4/[\text{Ca}^{2+}], \text{ or } [\text{HCO}_3^-] = [K_4/[\text{Ca}^{2+}]]^{1/2}$$

Likewise $[\text{CO}_3^{2-}]$ can be expressed in terms of $[\text{Ca}^{2+}]$ using the equilibrium expression for reaction [13-8]

$$[\text{CO}_3^{2-}] = K_{sp}/[\text{Ca}^{2+}]$$

Substituting these two expressions into the mass balance [13-12], and multiplying through by $[\text{Ca}^{2+}]$ gives

$$[\text{Ca}^{2+}]^2 = K_{sp} + [K_4[\text{Ca}^{2+}]]^{1/2} \quad [13-13]$$

The first term on the right hand side of equation [13-13] represents the contribution from reaction [13-8], and the second term the contribution from reaction [13-11]. The equation can be solved [with difficulty] algebraically, or [more simply] by successive approximations. Recognizing that $[\text{Ca}^{2+}]$ must be at least $10^{-4.0}$ M [the higher of our two approximate answers, above], we can plug this into the right hand side of equation [13-13], and take the square root to obtain a better estimate of $[\text{Ca}^{2+}]$. Repeating this procedure a few times produces a convergent answer, 1.30×10^{-4} [or $10^{-3.89}$] M. Thus the solubility of CaCO_3 is twice what it would be if carbonate were not a base [i.e. considering only reaction [13-8]].

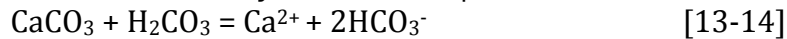
Having solved for $[\text{Ca}^{2+}]$, we can use this value to calculate the pH of the solution, using the equilibrium expression for reaction [13-11], and remembering that $[\text{HCO}_3^-] = [\text{OH}^-]$:

$$K_4 = [\text{Ca}^{2+}][\text{OH}^-]^2, \\ \text{or } [\text{OH}^-] = K_4/[\text{Ca}^{2+}]^{1/2} = [10^{-12.01}/10^{-3.89}]^{1/2} = 10^{-4.06}$$

Thus $\text{pOH} = 4.06$ and $\text{pH} = 9.94$. Dissolution of CaCO_3 produces a basic solution.

Worked Problem 13.3: CaCO₃ Solubility and CO₂

The solubility calculation is actually simpler for a solution exposed to the atmosphere, because then the only reaction of importance is



The equilibrium constant (which we call K_5) is

$$K_5 = [\text{Ca}^{2+}][\text{HCO}_3^-]^2/[\text{H}_2\text{CO}_3] = K_{\text{sp}}K_{\text{a1}}/K_{\text{a2}} = 10^{-4.41} \quad [13-15]$$

[Equation [13-14] is obtained by adding equations [13-8] and [13-10]. From the stoichiometry of reaction [13-14], we see that $[\text{HCO}_3^-] = 2[\text{Ca}^{2+}]$, and consequently $K_5 = 4[\text{Ca}^{2+}]^3/[\text{H}_2\text{CO}_3]$. $[\text{H}_2\text{CO}_3]$ is fixed by the atmospheric CO₂ concentration at $10^{-5.0}$ M [see p?]. Therefore

$$[\text{Ca}^{2+}] = [10^{-4.41}10^{-5.0}/4]^{1/3} = 10^{-3.33} \text{ M}$$

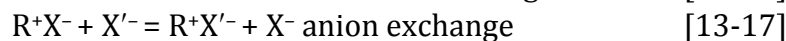
The pH is obtained from the H₂CO₃ acidity constant, recognizing that $[\text{HCO}_3^-] = 2[\text{Ca}^{2+}] = 10^{-3.03}$ M; then

$$\text{pH} = \text{p}K_{\text{a1}} - \log[\text{H}_2\text{CO}_3]/[\text{HCO}_3^-] = 6.40 - \log(10^{-5.0}/10^{-3.03}) = 8.37$$

Comparing these values with those obtained in Worked Problem 13.2, we see that equilibration with atmospheric CO₂ increases the calcium carbonate solubility by a factor of five, and lowers the pH by 1.5 units.

13S.2 Ion exchange; clays and humic substances

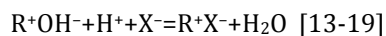
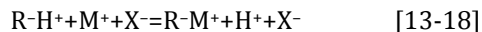
Many solids have ions that are loosely held at fixed charge sites. These can be exchanged with ions that are free in solution. The exchanging ions may be positively charged (cations) or negatively charged (anions):



In these reactions R represents a fixed charge site. It attracts ions of the opposite charge, the strength of attraction being proportional to the charge/radius ratio. (Multiple-charged ions can occupy more than one ion exchange site.) This is the underlying mechanism of *ion exchange resins*, organic polymers having numerous covalently attached charged groups.

Cationic resins can be strong or weak acid exchangers, depending on the proton affinity of the fixed anionic sites. Strong acid resins generally contain sulfonate groups, $-\text{OSO}_3^-$. Like sulfuric acid, protonated sulfonate groups readily give up their proton, when another cation is available for exchange. Weak acid resins generally contain carboxylate groups, whose pKa's, when protonated, are similar to acetic acid [~ 4.5]. Because of the relatively high proton affinity of the carboxylate group, other cations are readily displaced from the by protons. Likewise, anionic resins can be strong or weak base exchangers. Strong base resins have quaternary ammonium groups, $-\text{N}(\text{CH}_3)_3^+$ while weak base resins have

protonated amine groups, $-\text{NH}_3^+$, which have high affinity for hydroxide. Cation and anion exchange resins are widely used in tandem to deionize water:



The spent resins can be regenerated by washing them with strong acids and bases.

Because of their abundance in the earth's crust, silicates are the major component of soils (63% on average), and are responsible for most of the ion exchange capacity. Because of its closed three-dimensional network of oxygen atoms [Figure 13.1] silica itself [as found naturally in quartz] has no ion exchange sites. However, substitution of metal ions in the silica framework leaves uncompensated negative charges, because the charge on the metal ions [+3, +2 or +1] is less than the charge on silicon [+4] (counting the oxide ions as -2). These uncompensated charges are balanced by mobile cations, giving the silicate mineral cation exchange character.

Of special importance are the clays, which result from the weathering of primary silicate minerals, and are therefore abundant in soils. Clays contain sheets of polymerized silicate tetrahedra arranged in layers (Figure 13.3). Three of the oxygen atoms around each silicon atom are linked to neighboring silicon atoms in the sheet, while the fourth oxygen atom extends upward out of the sheet, bound to a second parallel layer. In the common clay minerals kaolinite and pyrophyllite, the fourth oxygen atom is bound to an aluminum ion, Al^{3+} (Figure 13.4). Aluminum prefers octahedral coordination and is surrounded by six oxygen atoms. In kaolinite, two of these oxygen atoms are provided by neighboring silicate groups, while the remaining oxygens come from hydroxyl groups; the aluminum hydroxyl groups form hydrogen bonds with adjacent silicate oxygen atoms to hold the layers together. In pyrophyllite, the aluminum octahedra are sandwiched between two silicate sheets (Figure 13.5); the next triple layer is held only weakly to the first one, since the facing silicate oxygen atoms lack protons with which to form hydrogen bonds. The interlayer space can be filled with water molecules, and pyrophyllite swells considerably in water. In many clays, some of the Al^{3+} ions are replaced by Fe^{3+} ions.

Other aluminosilicates have the kaolinite and pyrophyllite structures, but with some of the aluminum or silicon ions substituted by metal ions of lower charge. Thus, the common clay mineral montmorillonite has the pyrophyllite structure, but about one-sixth of the Al^{3+} ions are replaced with Mg^{2+} . Likewise, the illite clays share this structure, but Al^{3+} ions replace some of the Si^{4+} ions in the silicate sheet.

All of these substitutions of cations with lower charge produce excess negative charge, which is balanced by the adsorption of other cations, commonly Na^+ , K^+ , Mg^{2+} , or Ca^{2+} , in the medium between the aluminosilicate layers. These are the *base cations*, so called because their oxides are strong bases. They are readily exchanged for other cations in solution. The order of exchange depends upon the affinity of the cations for anionic sites on the clay compared to their attraction for

water molecules. Generally, aluminum cations are the most difficult to exchange and sodium cations the least difficult, with other ions between, in the order $\text{Al}^{3+} > \text{H}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+$. Since protons are more tightly held than most other cations, if the soil solution is acidic, the protons will exchange with the adsorbed cations. The exchange of protons for other ions increases both the solution's pH and its base cation concentration. Thus, like limestone, clays neutralize the acids in soil water while increasing the concentration of base cations.

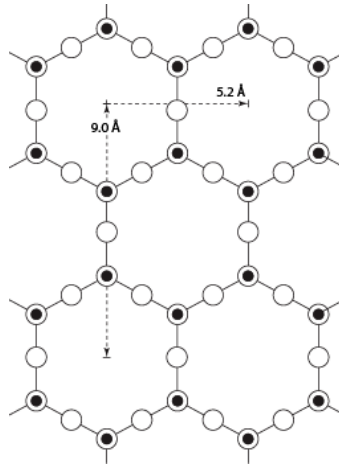


Figure 13.3 Layer structure of polymerized silicate tetrahedral. (The black circles represent silicon atoms and the open circles represent oxygen atoms. Each silicon atom is tetrahedrally bound to four oxygen atoms. The oxygen atoms shown superimposed on the silicons are directed upward and bound to a second parallel layer.)

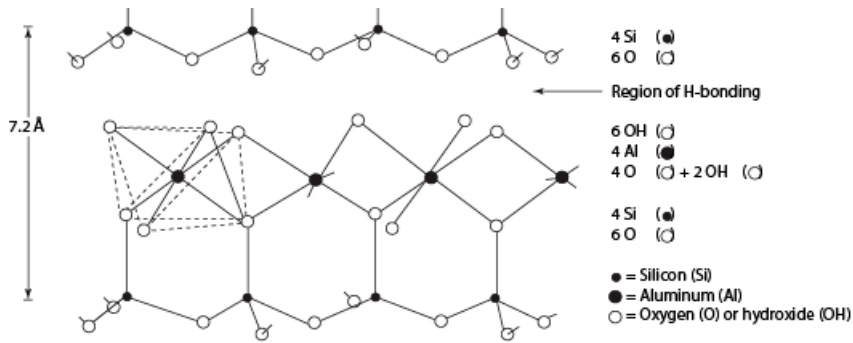


Figure 13.4 Structure of kaolinite, $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$. The plates contain phyllosilicate sheets bound to octahedral aluminum layers. (Dashed lines show six-fold coordinate positions in octahedral layer.) The distance between two successive plates is 7.2 Å.

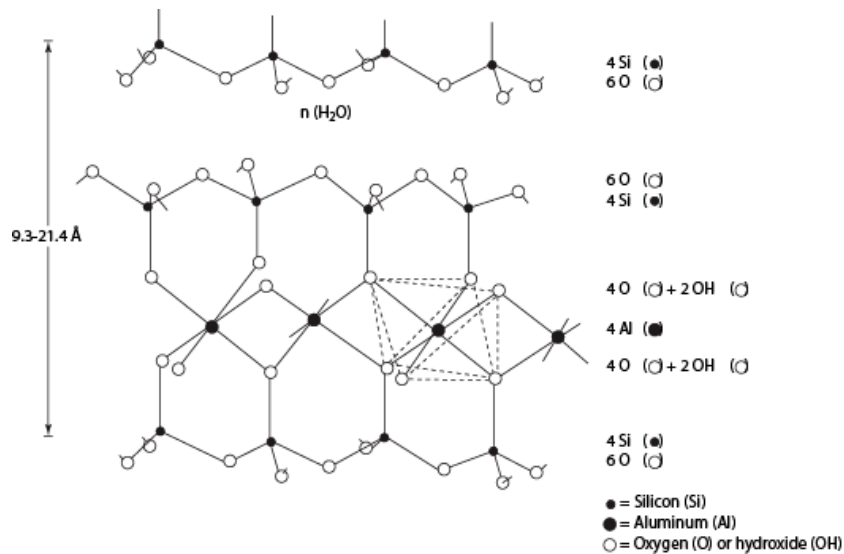


Figure 13.5 Structure of pyrophyllite, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$. The plates contain octahedral aluminum layers sandwiched between two phyllosilicate sheets. The distance between the plates can vary up to 21 Å, depending on the amount of water present between plates.

Soil also contains organic matter, the humus, consisting of the remains of decomposed vegetation. The remains that are most resistant to degradation, and therefore most abundant in soils, are complex polymeric materials, which have a high content of aromatic groups [as does lignin, see p. ?]. Partial oxidation in the soil introduces many carboxylate and phenolic OH groups [see **Figure 13.6** for schematic structures]. Collectively these are called *humic substances*, and are sometimes divided into *humic acid* and *fulvic acid*, based on their response to extraction by strong base and subsequent acidification. Humic acid is the non-extractable fraction, while humic and fulvic acid both dissolve in strong base. Humic acid precipitates upon subsequent acidification, while fulvic acid remains in solution. In the soil, the numerous carboxylate groups provide cation exchange sites, complementing those of the clays.

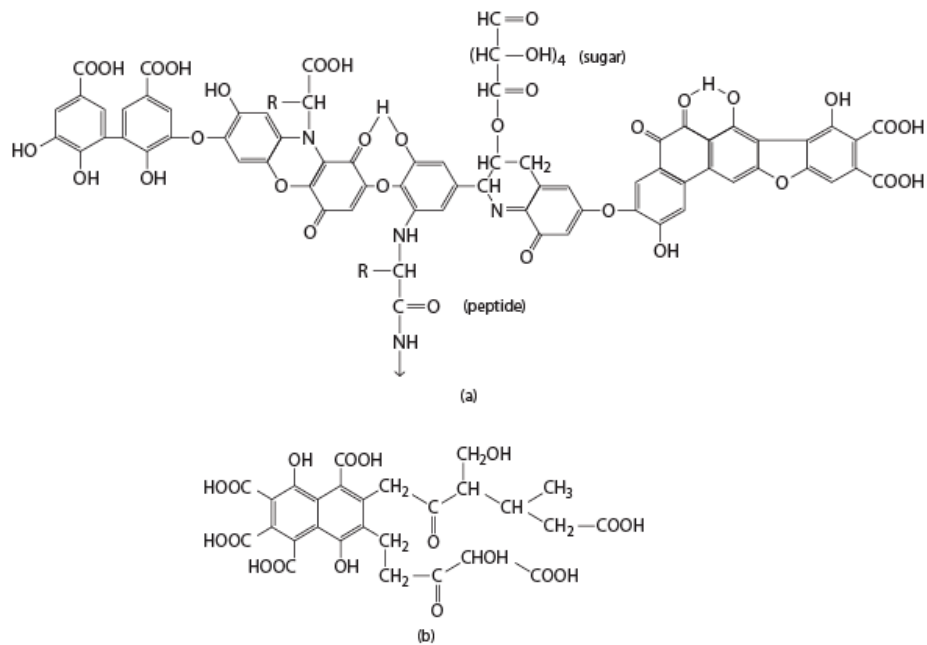


Figure 13.6 (a) Model structure of humic acid showing sugar and peptide groups, free and bound phenolic OH groups, and carboxylates (-COOH); (b) model structure of fulvic acid containing both aromatic and aliphatic components extensively substituted with phenolic and carboxylate functional groups. The hydrogen (H⁺) on the carboxylate group can exchange with base cations. Because of the abundance of carboxylates, humic soils have high cation exchange capacities.

13.3 Effects of Acidification

13.3a Ocean Acidification

An ominous consequence of this simple chemistry is that sea creatures may have difficulty making their calcium carbonate shells as the atmospheric CO₂ rises. The oceans are currently saturated with respect to CaCO₃, but the rate of shell production depends on the carbonate concentration, which decreases as CO₂ rises and the pH falls. Experiments in controlled environments have demonstrated that adding CO₂ to sea-water slows the rate at which coral and reef-building algae secrete CaCO₃. Figure 13.7 illustrates the dramatic inhibition of sea urchins CaCO₃ spines when CO₂ is elevated.

In a field study at a Pacific Ocean site where a volcanic plume of liquid CO₂ acidifies the seawater locally naturally acidified seawater to pH values between 5.4 and 7.3, mussels were found to grow half as fast as normal, and had shells that were thin enough to see through.[^]

[^] Tunnicliffe, V. *Nature Geoscience*, (2009) **2**, 344 – 348.

The geological record indicates that ocean pH held constant at 8.2 during the last 600,000 years, but has dropped to 8.1 since 1800. If atmospheric CO₂

concentration doubles, $[H^+]$ will be halved, and the pH will drop further, to 7.8. The disruption ocean life could be extensive. It is believed that growth of coral reefs is already affected by ocean acidification.

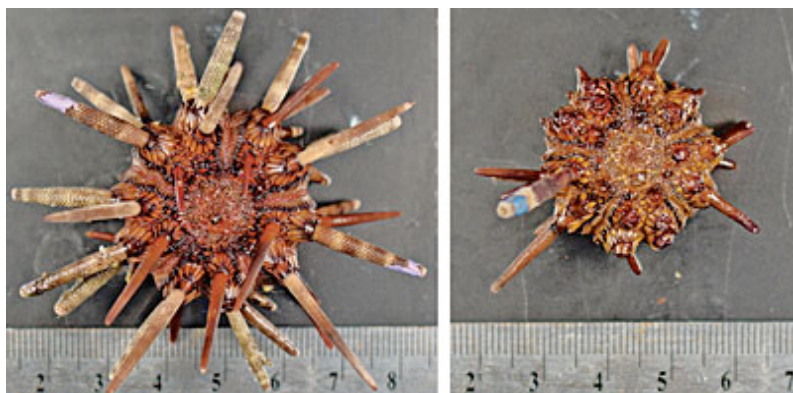


Figure 13.7 Sea urchins grown in seawater acidified with 400 ppm CO_2 (left), which is the current concentration in the ocean, versus 2,850 ppm CO_2 (right). Size measured in centimeters. *Source:* R. Petkewich (2009). *Off-Balance Ocean: Acidification from absorbing atmospheric CO_2 is changing the ocean's chemistry. Chemical & Engineering News*, 87:56-58. Photo by Justin Reis, University of North Carolina Chapel Hill.

13.3b Soil neutralization

Figure 13.8 diagrams the acid-base reactions that occur after rain falls to the ground. Initially the pH can diminish, because topsoil contains large amounts of CO_2 due to bacterial decomposition of the organic matter, up to 100 times the concentration of CO_2 in the atmosphere. In addition, plants exude a variety of organic acids, and the decay of plant matter produces other acids *en route* to the eventual conversion of the organic molecules to CO_2 . pH values in the topsoil are frequently below 5.

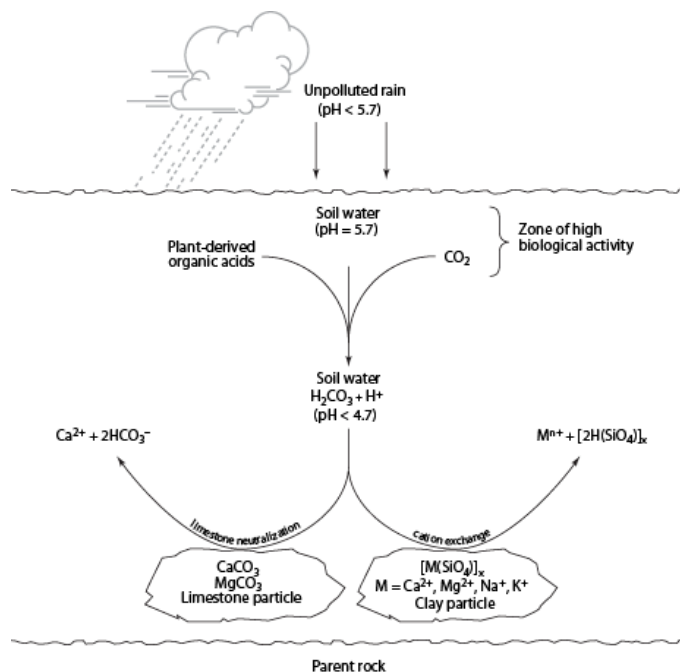
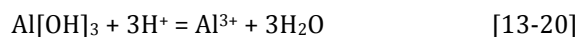


Figure 13.8 Percolation of rainwater through soil and neutralization by limestone and clays.

As the water percolates into the mineral layers, neutralization reactions come into play. In soils containing limestone [*calcerous* soils], neutralization raises the pH toward 8.4 [see Worked Problem 13.3]. The effectiveness of this reaction is reflected in the widespread practice of *liming* [mixing crushed limestone into the soil] agricultural fields, as well as lawns and gardens, in order to raise the pH of acidic soils.

When limestone is absent, neutralization occurs via exchange of protons for the base cations on ion exchange sites of clay particles and of the humus. The number of exchangeable cation sites is the *cation exchange capacity* [CEC], measured in units of acid equivalents [eq] per square meter of soil. The fraction of the sites occupied by base cations, rather than by H⁺, is called the *base saturation* [β]. These ion exchange sites consist of anionic oxygen atoms bound to the silicate lattice [or organic acid anions in the case of humus] and are much less basic than is the carbonate ion. Consequently the pH rises much less in non-calcerous than in calcerous soils; typically the pH in non-calcerous soils is about 5.5.

Because the ion exchange sites are on the particle surface, the CEC is limited, and is much less than the neutralizing capacity of calcerous soils. However, the CEC is slowly replenished by silicate weathering reactions, such as reaction [13-2] which release additional base cations, and provide new ion exchange sites. In some of the weathering reactions Al³⁺ is also released from the aluminosilicate framework of clays. Because Al(OH)₃ has a very low solubility, it precipitates at pH values above about 4.2 and stays bound to the soil particles. If soil acidification exceeds the CEC, so that nearly all the base cations are replaced by protons [β declines toward zero], then the pH drops below 4.2 and aluminum is solubilized.



13.3c Hardness and detergents

The neutralization reactions that raise the pH of natural water as it percolates through the soil (**Figure 13.8**) also bring into solution appreciable quantities of calcium and magnesium ions. Water with relatively high concentrations of Ca^{2+} and Mg^{2+} is considered “hard,” while water with low concentrations is “soft.” Soft water also has lower pH because the low Ca^{2+} and Mg^{2+} concentrations reflect poor availability of limestone or clays for neutralization.

The hard and soft appellations reflect the fact that the doubly charged Ca^{2+} and Mg^{2+} ions can precipitate detergents. Detergents are molecules with long hydrocarbon chains and ionic or polar head groups (**Figure 13.9a**). When added to soft water, the detergent molecules aggregate into micelles (**Figure 13.9b**), with the hydrocarbon tails pointing to the inside and the polar groups pointing out toward the water. The hydrophobic interior of the micelles solubilizes grease and dirt particles and removes them from clothing, dishes, or other items being washed. In soft water, the micelles float freely and are prevented from aggregating with one another by the mutual repulsions of the polar hydrophilic head groups.

This solubilization process is prevented by hard water. The polar head groups of most detergents are negatively charged; they interact with divalent cations such as Ca^{2+} and Mg^{2+} and precipitate. The micelles are then unavailable for solubilizing dirt; worse still, the precipitates themselves tend to be scummy and stick to the items being washed. Consequently, in areas with hard water, a clean wash requires the addition of agents—called *builders* in the laundry trade—that tie up polyvalent cations and thereby prevent them from precipitating the detergent.

Detergent products contain a variety of kinds of builders. One class comprises *chelating agents*, molecules with several donor groups that can bind the cations through multiple coordinate bonds. A particularly effective chelating agent is sodium tripolyphosphate (STP), which is shown bound to a Ca^{2+} ion in **Figure 13.10**. This compound is relatively inexpensive and has the advantage that it rapidly breaks down in the environment to sodium phosphate, a naturally occurring mineral and nutrient for plants. However, STP-containing detergents release sodium phosphate into natural bodies of water and can stimulate plant growth, leading to eutrophication (see discussion beginning on p. ?). Because of the importance of limiting phosphorus inputs to streams and lakes, phosphates have been banned in the U.S. for use in laundry detergents and will be phased out of automatic dishwashing detergents by 2010. Several European countries have also banned the use of phosphates in laundry detergents.

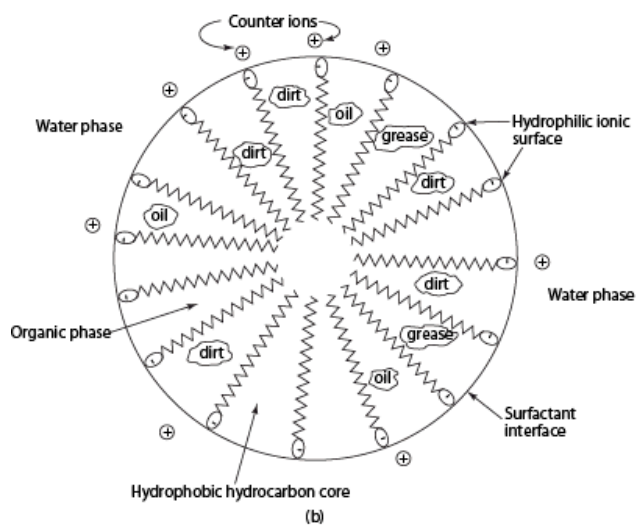
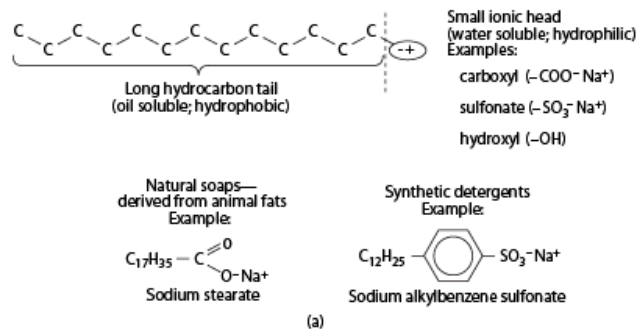


Figure 13.9 (a) Structures of detergent molecules; (b) schematic diagram of a detergent micelle.

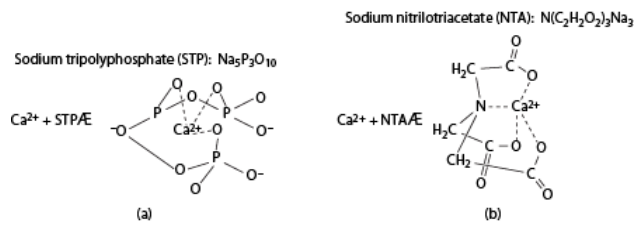


Figure 13.10 Chelating agents: chemicals that tie up positive ions in solution so they can no longer react with detergents (a) sodium tripolyphosphate (STP); (b) sodium nitrilotriacetate (NTA).

A variety of alternative chelating agents have been explored, such as sodium nitrilotriacetate, NTA (**Figure 13.10**). NTA is not widely used currently, partly because of cost, and partly because of concern that NTA does not break down as readily as STP does and therefore might mobilize metals other than calcium and magnesium. The most successful alternative builders are *zeolites*, synthetic aluminosilicate minerals that can trap Ca^{2+} or Mg^{2+} by ion exchange, releasing Na^+ ions in their place. Zeolites are used in place of STP in U.S. laundry detergents.

A new development is the addition of enzymes to detergent formulations. Mostly these are *protease* enzymes, harvested from bacteria, that digest the protein component of stains (blood, milk, sweat, grass, etc.). *Amylase* is also added to digest starches. The added enzymes reduce the amount of surfactant and builder required for a clean wash, and more important, they operate at low temperatures ('cold water wash'), saving the energy otherwise required to heat the wash water.

13.3d Acid deposition and watershed buffering

As described in Part I, the atmosphere receives substantial inputs of SO_2 and NO_x from both natural and anthropogenic sources. These emissions are cleared from the air within a few days by oxidation reactions and subsequently transfer to the soil, either directly by dry deposition in aerosols, or indirectly by wet deposition in rainfall. Such reactions are vital to the health of the biosphere because they cleanse the air of noxious fumes. If SO_2 and NO_x accumulated in the atmosphere as CO_2 does, the air would quickly become toxic.

However, the cleansing of the atmosphere transfers sulfuric and nitric acids to the soils. Hence, soils can be described as *sinks* or *reservoirs* for atmospheric pollutants. Pollutants emitted to the air flow through the environment, mediated by a series of physical and chemical processes, as illustrated schematically in **Figure 13.11**. The first step is air transport and then deposition onto soil (1). Soils, in their capacity as *chemical filters*, may adsorb, neutralize, or otherwise retain and store the pollutant. When buffering capacities are diminished, the soil may release the pollutant to rivers and lakes (2a) or to the groundwater (2b). Eventually, pollutants are discharged to the oceans through stream (3a) and subsurface (3b) flow, and deposited in the ocean sediment (4), their ultimate repository.

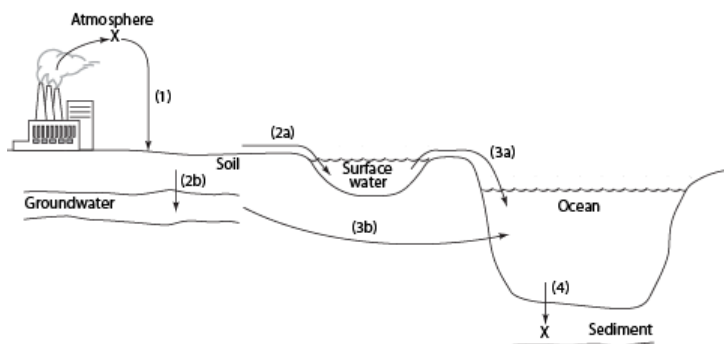


Figure 13.11 Flow of pollutant X from sources to sinks.

The effectiveness of the soil as a chemical filter of acidic inputs depends upon its buffering capacity and the rate of acid deposition. Although the buffering capacity of most soils is sufficient to neutralize naturally occurring acids, over time the capacity can be overwhelmed by high inputs of acid deposition. **Figure 13.12** illustrates schematically the course of events as soil is continuously acidified. If limestone is present, the pH is initially maintained at around 8, through the dissolution of carbonate. When the limestone is dissolved away, then the pH drops to about 5.5 as acid displaces the base cations in the soil. When these are all displaced, the pH falls to around 4,

where the $\text{Al}[\text{OH}]_3$ is gradually dissolved. Thus there are three distinct buffer regions, as soil is titrated by protons.

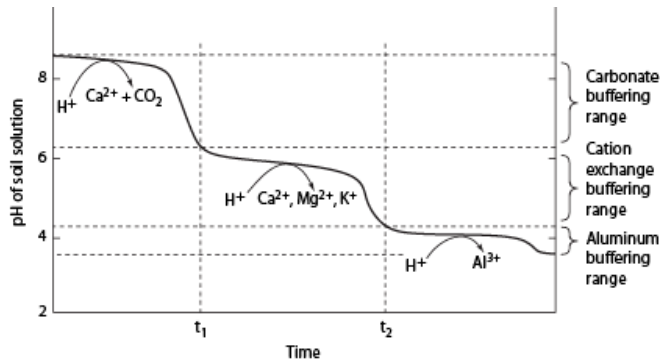


Figure 13.12 Scheme showing progression of decline in soil solution pH over time in response to atmospheric acid inputs. For a given soil, the time-scales over which the soil solution passes from one buffering range to the next depends on the intensity of acid deposition and the concentration of exchangeable cations. Arrows indicate the chemistry by which soils retain H^+ from the soil solution by exchanging it for cations. The period from t_1 to t_2 is the time over which soils lose 90-95 percent of their original exchangeable base cations. *Source: W.M. Stigliani and R.W. Shaw (1990). Energy use and acid deposition: The view from Europe. Annual Review of Energy 15:201-216.*

Figure 13.12 can also represent the fate of a watershed which is subject to continuing inputs of acid. The pH can stay fairly constant, at either the carbonate or the silicate buffer pH, for extended periods of time, and then drop rapidly when the buffer capacity is exceeded. It is hard to predict when this will happen. The length of time depends upon many factors, including the rate of deposition, the nature of the soil, the size of the watershed, and the flow characteristics of the lake or groundwater.

One case where the historical record of acidification has been well documented, however, is the watershed of Big Moose Lake in the Adirondack Mountains of New York state. This area has received some of the highest inputs of acid deposition in North America because it is downwind from western Pennsylvania and the Ohio Valley, historically the industrial heartland of the United States. Pollutants carried by the westerly winds are trapped in the mountains and deposited via wet and dry deposition.

The difficulties of recognizing acidification while it is occurring are illustrated in **Figure 13.13** which shows the historical trends in Big Moose lake water pH (dashed line), SO_2 emissions upwind from the lake (solid line), and the extinction of different fish species. The Adirondack watersheds lie on granitic rock, and are without limestone. The pH of the lake remained nearly constant at around 5.6, the silicate buffer value, over the entire period from 1760 to 1950. Then, within the space of 30 years, from 1950 to 1980, the pH declined more than one whole pH unit to about 4.5. The decline in pH lagged behind the rise in SO_2 emissions by some 70 years, and the peak years of sulfur emissions preceded the decline in pH by 30 years. The deposition rate is estimated to have been about $2.5 \text{ grams of sulfur m}^{-2}\text{yr}^{-1}$ during the peak period. These quantities, deposited year after year, were large enough to deplete the capacity for base cation exchange in the watershed. Thus, beginning around 1950, atmospheric acid deposition

moved through the buffer-depleted soils of the watershed and percolated into the lake with diminished neutralization (**see problem ?**). At that point, acid-sensitive fish species such as smallmouth bass, whitefish, and longnose sucker began to disappear, followed in the late 1960s by the more acid-resistant lake trout.

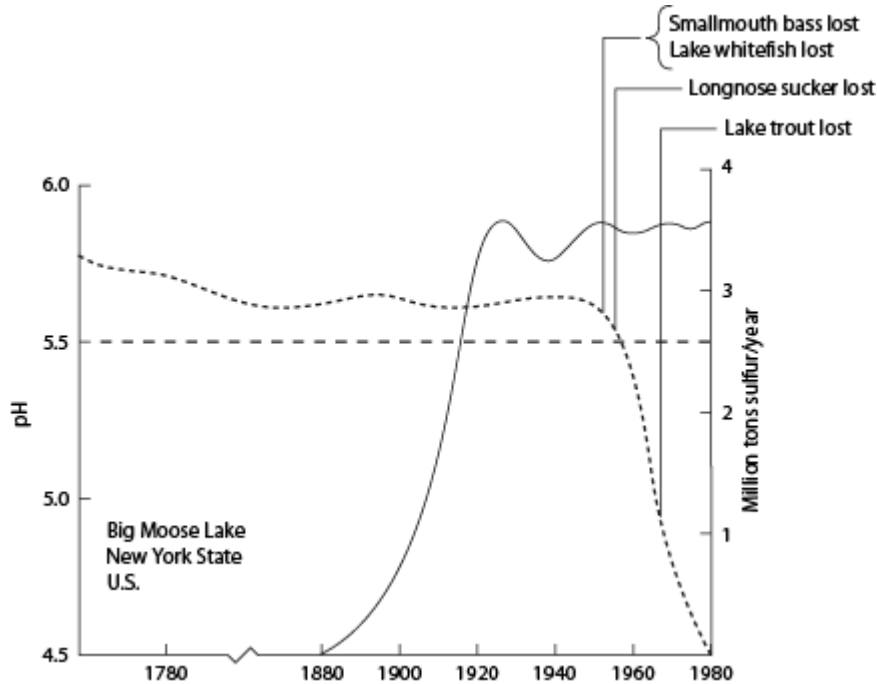


Figure 13.13 Trends in lakewater pH (dashed curve), upwind emissions of SO_2 from the U.S. industrial Midwest (solid curve), and fish extinctions for the period from 1760 to 1980. *Source: W.M. Stigliani (1988). Changes in valued capacities of soils and sediments as indicators of nonlinear and time-delayed environmental effects. Environmental Monitoring and Assessment 10:245-307.*

From the shape of the historical pH trend, we can see that Big Moose Lake was the subject of an inadvertent titration experiment conducted over four generations of industrial activity. The coal-driven industrialization of the Ohio Valley, upwind from the lake, supplied the acid inputs, mostly as sulfuric acid formed from SO_2 released during coal combustion. The soils of the watershed provided the supply of buffering chemicals. Thus, the watershed's natural buffering capacity delayed recognition of the deleterious effects of coal burning for about three generations. During this time, there was no direct evidence of how pollution was affecting the pH of lake water or fish mortality. As this example suggests, polluting activities may be far displaced in time from their environmental effects.

13.3e Ecosystem effects of acid rain

Although loss of fish in acidified lakes is a dramatic indicator, ecosystem effects of acid rain are much more widespread. Painsstaking studies at Hubbard Brook Experimental Forest, in New Hampshire, have revealed that concentrations of calcium and magnesium have been lowered to half their historic values and that the overall

growth of vegetation is at a standstill. Studies at many other sites in the northeastern states likewise show reductions in nutrient cation levels, and also the release of aluminum, which is sometimes found precipitated on the rootlets of trees, blocking nutrient uptake. In Vermont forests acid fogs and rain have been found to leach calcium directly from spruce needles, leaving the trees susceptible to drought and insects. Similar effects are now being reported in the Southeast of the U.S., some 20 years after they appeared in the Northeast. The delay is attributed to the buffering effect of thicker southern soils, which are now becoming saturated with acid.

Over the past three decades progressively tougher pollution rules have reduced U.S. emissions of SO_2 by about 68%, but ecologists estimate that additional reductions will be required to permit affected soils to regenerate the base cation levels needed for healthy trees. Meanwhile, the nitric acid component of acid rain is receiving increasing attention, particularly in the Western U.S., where low-sulfur coals minimize SO_2 emissions, but where increasing population and traffic (as well as the manure from the region's animal feedlots), have led to increased NO_x in the atmosphere. Ancient spruces in the Rocky Mountains which are downwind of populous areas have been show high levels of nitrogen and low levels of magnesium in their needles. Nearby streams, which are usually nutrient-poor, show populations of diatoms shifting toward species that do better in nitrate-rich waters.

Damage from acidification is magnified when soils are also polluted by toxic metals such as cadmium, copper, nickel, lead, and zinc. As cations, these metals compete with hydrogen and the base cations for cation exchange sites. At high pH, metal ions in well-buffered soils are generally retained at the exchange sites; their concentrations in soil solution are low. However, as the pH declines from 7 to 4, the leaching velocity at which an ion migrates through the soil may increase by an order of magnitude as shown by the example of cadmium (**Figure 13.14**). Thus, at near neutral pH, the soil will accumulate heavy metals such as cadmium, only to release them as the soil acidifies. Once in the aqueous phase, cadmium ions are mobile and biologically active. They can be transported to lakes via surface or subsurface flow, transferred to groundwaters, or taken up by vegetation, with toxic effects. Al^{3+} is also toxic to plants and aquatic organisms. Some of the deleterious effects of strong acidification are probably due to the Al^{3+} leached from clay particles in the soil.

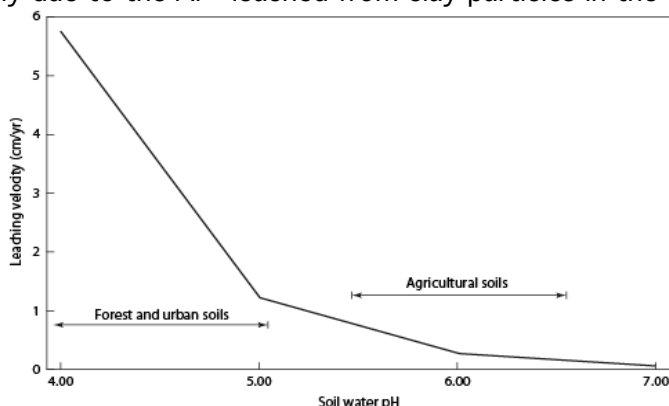
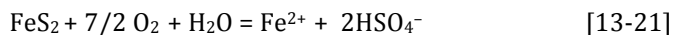


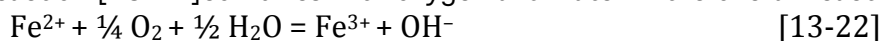
Figure 13.14 Leaching velocity of cadmium in soil as a function of soil water pH. *Source:* W.M. Stigliani and P.R. Jaffee (1992), private communication (Laxenburg, Austria: International Institute for Applied Systems Analysis).

13.3f Acid mine drainage

A problem related to acid rain is acid mine drainage. Coal mines, especially those that have been abandoned, are known to release substantial quantities of sulfuric acid and iron hydroxide into local streams. The first step in the process is the oxidation of pyrite (FeS_2), which is common in underground coal seams:



This reaction is analogous to the first step in the generation of acid rain, in which sulfur is oxidized during coal combustion. In acid mine drainage, however, this step is mediated under aerobic conditions by the bacterium *thiobacillus ferrooxidans*, which oxidizes FeS_2 as an energy source much the same way that other aerobic bacteria oxidize organic carbon (CH_2O) in respiration reactions (p.?). The oxidation step occurs spontaneously at ambient temperatures once iron sulfide, which is stable in the absence of air, is exposed to the atmosphere. In the second step, the ferrous iron (Fe^{2+}) formed from reaction [13-21] combines with oxygen and water in the overall reactions:



The sum of reactions [13-21], [13-22] and [13-23] yields the following reaction:



Thus, one mole of pyrite produces two moles of sulfuric acid and one mole of ferric hydroxide, which is removed from solution as a brown precipitate. The pH of streams receiving this drainage can be as low as 3.0.

These reactions continue long after coal mining operations have ceased. The resulting pollution problem can be quite severe locally; in coal mining areas, streams are often highly polluted by sulfuric acid. The problem is difficult to prevent because sealing up mines effectively is arduous and expensive. Since coal mining is a major activity on most continents, the problem of acid mine drainage has global implications.

13.3g Global acidification

Thus far we have been discussing acidification on local and regional scales. Acid mine drainage is tied to particular watersheds; acid rain depends upon industrial activity and prevailing weather patterns. But acid deposition on a global level from industrial sources is of the same order of magnitude as deposition from natural sources (**Table 13.2; see problem 11**). Acid deposition is not the whole story, because there are also natural and anthropogenic sources of alkaline chemicals in the atmosphere. These include ammonia (NH_3) and alkaline particles derived from ash, as well as windblown alkaline minerals. These chemicals have been crudely estimated to neutralize between 20 and 50% of the generated acidity. The atmosphere has acted as an acidic medium throughout geologic time, but natural sources of acidity, although of the same order of magnitude as anthropogenic sources, are spread evenly across the globe. Polluting sources are concentrated near industrial and urban centers, with levels of acidity exceeding 50 to 100 times the natural background. It is the excessive concentration of acidity in particular regions that causes problems for the biosphere.

Table 13.2 Estimated natural and anthropogenic sources of global atmospheric acidity

Source	10^{12} moles of H^+ generated per year
NATURAL	
Unpolluted rainwater	1.0
Lightning*	1.4
Volcanoes†	1.3
Biogenic sulfur	4.1
TOTAL NATURAL	7.8
POLLUTION	
Coal combustion/metal smelting†	5.8
Combustion processes ⁸	1.4
TOTAL FROM POLLUTION	7.2

* Refers to acidity generated from NO_x emissions.

† Refers to acidity generated from SO_2 emissions.

Source: Adapted from W.H. Schlesinger (1991). *Biogeochemistry, an Analysis of Global Change* (San Diego, California: Academic Press, Inc.).

Problems:

1. (a) The total amount of base in a water sample can be determined by titration with standard acid, and is usually reported as the *alkalinity*, in equivalents of acid per liter (eq/l). If the alkalinity of carbonate-containing sample is 2.0×10^{-3} eq/l, and the pH is 7.0, what are the concentrations of OH^- , CO_3^{2-} , HCO_3^- and H_2CO_3 ? [see pp. ?? for required equilibrium constants].

(b) How do these concentrations change if the pH of the sample increases to 10.0 as a result of photosynthesis by algae (for simplicity assume no input of CO_2 from the atmosphere). What weight of biomass, $[CH_2O]$, is produced.

2. How much Fe^{2+} could be present in water containing 1.0×10^{-2} M HCO_3^- , without causing precipitation of $FeCO_3$ [$K_{sp} = 10^{-10.7}$]?

3. Calculate the solubility of silver (II) carbonate, $AgCO_3$ ($K_{sp} = 6.2 \times 10^{-12}$) in water, assuming that most of the carbonate ion produced reacts with water to form bicarbonate ion. Then calculate the solubility assuming that none of the carbonate reacts with water to form bicarbonate. How do your results differ based on the two different assumptions?

4. If groundwater with alkalinity of 4.0×10^{-3} eq/l, pH = 7.5 and $[Ca^{2+}] = 2.0 \times 10^{-3}$ M is pumped to the surface and exposed to the atmosphere, how would its composition change?

5. Describe the three major buffer ranges for neutralizing acidic inputs to soils. For each of the ranges, include in your description: (1) the pH range over which the buffer operates; (2) the major chemical component(s) that participates in the buffering reactions; and (3) the chemical reaction by which H^+ is neutralized.

6. Describe the differences in humin, humic acid, and fulvic acid. Which of the three has the highest carbon content?

7. Why is the process of acid deposition beneficial from the point of view of air quality? How does this process transfer a short-term air-pollution problem into long-term problems of soil and water pollution?

8. Why is carbonic acid effective in weathering parent soil rock, but not an important factor in lake acidification?

9. (a) With reference to Figure 13.13, assume that the average annual deposition of sulfur in the watershed of Big Moose Lake between 1880 and 1920 was 0.8 g S/m^2 , and from 1921 to 1950 it was 2.5 g S/m^2 . Calculate the cumulative acid equivalents (eq) per m^2 that were deposited in the watershed over the entire period 1880 to 1950.

(b) Assume that the watershed soils buffered acidity via exchange reactions with base cations on clay mineral surfaces. Assume further that base saturation (β) declined from 50% in 1880 to 5% in 1950. Calculate the total Cation Exchange Capacity (CEC_{tot}), and the buffering capacity ($\text{CEC}_{\text{tot}} \propto \beta$) in 1880 (in units of eq/m^2). Also assume that the silicate buffer rate (br_{Si}), which replenishes the base cations in soil from weathering of silicate, was negligible over this period.

(c) Do the same calculation as in 2(b), but assume br_{Si} was equal to $0.02 \text{ eq m}^{-2} \text{ y r}^{-1}$ over the time scale from 1880 to 1950. What would you expect the pH of the soil water to be when the base saturation approaches 5%.

10. Write the equations for the oxidation of pyrite (FeS_2) and give two examples of anthropogenic activities that can initiate the oxidation. What is the environmental effect manifested by pyrite oxidation?

11. (a) Show how the numbers given in Table 13.2 were calculated for natural sources. Make the following assumptions: the pH of unpolluted rainfall is 5.7, and annual global precipitation is $496,000 \text{ km}^3/\text{y r}$; production of NO_2 from lightning is $20 \times 10^{12} \text{ g N/yr}$; production of SO_2 from volcanoes is $20 \times 10^{12} \text{ g S/yr}$; biogenic production of dimethylsulfide (DMS) and H_2S is $65 \times 10^{12} \text{ gS/yr}$.

(b) Calculate moles of hydrogen ions per year generated from coal burning and smelting, assuming this activity generates about $93 \times 10^{12} \text{ g S/yr}$. Assume combustion processes from all activities generate about $20 \times 10^{12} \text{ g N/yr}$.

(c) Calculate the acid-neutralizing capacity of the atmosphere due to generation of ammonia (NH_3). Assume that natural and anthropogenic sources each generate about $60 \times 10^{12} \text{ gN/yr}$. Calculate the total *net* generation of H^+/yr from both natural and anthropogenic sources.

(d) Calculate the average moles $\text{H}^+ \text{m}^{-2} \text{yr}^{-1}$ from natural sources. (The area of the globe is $510 \times 10^{12} \text{ m}^2$.) Calculate the average moles $\text{H}^+ \text{m}^2 \text{yr}^{-1}$ in

industrialized regions of the globe. (Assume that the area of industrialized regions is $11.75 \times 10^{12} \text{m}^2$.)