# Chapter 2
# Geochemical Reactions

## GEOCHEMISTRY AND WATER QUALITY

Since ancient times, cities and civilizations have been built around reliable sources of potable water. Constantinople, now Istanbul, has even today at its heart a deep cistern protected by surrounding ramparts and stone arches that supplied groundwater to its population. Jiao (2007) describes a 5600 year old well in Zhejiang Province, China with walls and roof to protect its valuable groundwater source. The *aflaj* of Oman, horizontal wells tunneled kilometers through sand, gravel and rock, have drained fresh groundwater from beneath the parched landscape to the coastal cities since the times of Sindbad. The early hydrogeologists who built these water supply systems had a concern for not just the quantity of water they could tap, but also its quality. However, it has only been in the later half of the $20^{th}$ century that we have developed a fuller understanding of processes that control the quality of water.

Why *geo*chemistry? In natural waters, it is the interaction of the hydrosphere with the geosphere that controls the chemistry of surface waters and groundwaters. Biological processes play a key role too, and so the *bio* prefix is often added. In this text, all processes related to the Earth, organic and inorganic are implied in the term geochemistry. These processes include dissolution of air-borne material and gases, weathering at the Earth's surface, biodegradation and nutrient cycling in the soil, mineral dissolution in the subsurface, and mixing with seawater or deep crustal water.

Human activity also plays a major role in the quality of water. Contaminants contribute to the geochemistry of water through industrial, municipal, agricultural and other activities. The modification of landscapes can initiate geochemical processes, such as the release of metals and acidity in mining camps, salt build-up in irrigated agricultural settings, and loading of organics from landfills. Aqueous geochemistry is then the study of the natural and anthropogenic processes that affect the quality of surface and groundwaters.

These processes are examined as reactions that transfer mass between reactants and products. Some reactions such as the dissolution of high temperature minerals like olivine, or the oxidation of pyrite, proceed in one direction only at low temperature. Others, like calcite dissolution are reversible and precede either forwards or backwards depending on the availability of reactants and the concentrations of products as governed by the law of mass action.

### *The law of mass action, geochemical reactions and the activity of solutes*

Geochemical reactions involve the transfer of mass between reactants as solids or solutes with given thermodynamic concentrations or *activities* [$a_{reactant}$] that are transformed into various products [$a_{product}$]. From an initial condition where the system includes only reactants, the reaction proceeds in a forward direction and reactants accumulate in the system:

$reactants \ \rightarrow \ products$ non-equilibrium – net mass transfer from reactants to products

$reactants \ \Leftrightarrow \ products$ equilibrium – no net transfer of mass

The law of mass action holds that reactions will proceed to towards a state of equilibrium between reactants and products that is defined by a thermodynamic constant that is unique to that given reaction:

$$K_{reaction} = \frac{activity\ of\ products}{activity\ of\ reactants} = \frac{a_{products}}{a_{reactants}}$$

Use of a reaction constant as defined by the law of mass action allows geochemists to model a system and evaluate which reactions are possible and which way they will go under given conditions.

The law of mass action applies to the full range of geochemical reactions, and allows us to quantify a reaction based on thermodynamics — the gain and release of energy associated with the transfer of mass between reactant and product reservoirs. Low temperature aqueous geochemistry includes the range of aqueous reactions between solids, solutes, gases, isotopes and water. The reactants and products can be both inorganic (e.g. calcite [$CaCO_3$] or dissolved sulfate [$SO_4^{2-}$]) and organic (e.g. carbohydrate [$CH_2O$] or acetate [$CH_3COOH$]). Low temperature geochemical reactions can often be abiotic, although many are mediated by bacteria, and some involve the degradation of organic substrates. There are four classes of reactions that we will review here:

> *Dissociation reactions* involve the transfer of mass through the formation and breaking of largely ionic bonds between solutes, acids and bases.
> *Oxidation-reduction reactions* involve the exchange of electrons between electron donor species and electron acceptors.
> *Gas solubility* reactions are physical, rather than chemical, and considers the total and partial pressures of gases in an aqueous system.
> *Isotope fractionation* reactions are those that partition isotopes of a compound into the reactant or product reservoir during a chemical reaction.

Fig. 2-1  Aqueous reactions involve transfers of solutes between solid and aqueous phases, as well as between aqueous and gaseous phases.

### Bonding

Elements seek to complete their valence electron shell through bonding with other elements. Bonding is due to the coulomb attraction between the negatively charged electron shell of one atom and the positive nucleus of another. This force of attraction falls off with the square of the inter-atomic distance. However, too close and the repulsive force between the two positively charged nuclei exceeds the coulomb force of attraction. The point of balance between these forces occurs at a distance of minimum potential energy in the molecule. This inter-atomic distance is the bond length, as shown in Fig. 2-2. Breaking the bond requires energy, usually as heat. Similarly, forming the bond releases heat to the surrounding system.
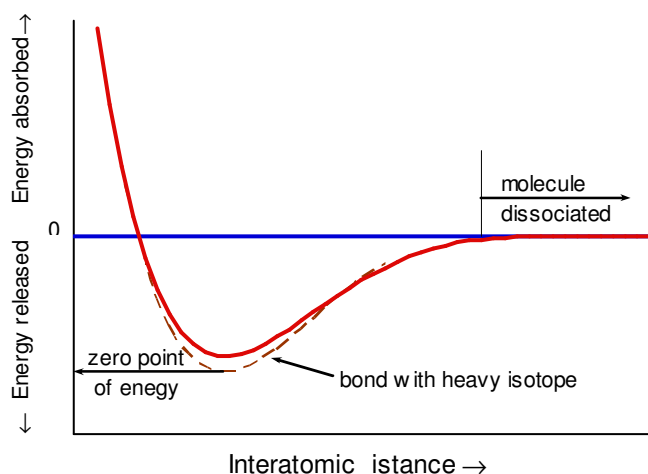
Fig. 2-2  Potential energy gained and released according to inter-atomic distance between bonded atoms. The bond length is the distance at which this energy is minimized. The dashed potential energy curve is drawn for a bond that includes a heavy isotope, showing that while the bond length may be the same, the bond strength is greater.

The atoms of different compounds are typically bonded by varying degrees of electron sharing, ranging from ionic, where no electrons are shared, to covalent, where the valence electrons are equally shared in the orbitals of the outer shell of both atoms. The degree of covalent bonding depends on the difference in *electronegativity* of the elements involved. Electronegativity can be considered to be the force with which an atom can attract electrons to its valence shell. Electronegativity increases towards the right side of the Periodic Table for elements, but decreases down the Periodic Table. Thus, the halides (F, Cl, Br, I) and the light non-metals (B, C, N, O) have the highest electronegativities, while the alkalis (Li, Na, K, Rb, Cs) have the lowest.

In bonds between atoms with strongly contrasting electronegativities, the valence electrons orbit the atom with the strongest electronegativity, giving it a negative charge (the anion) and leaving the other atom stripped of its valence electrons and so carrying a positive charge (the cation). They bond because of the electrostatic attraction of the opposite charges, and this is an *ionic* bond. Halite — NaCl is the most common example of ionic bonding, where $Na^+$ has shed its outer orbit electron and $Cl^-$ has gained an electron to fill its outer orbit. Ionic bonds are weak, and such minerals have high solubilities.

In compounds where the bonding elements have similar electronegativities, ownership of the valence electrons is not so clear, and so they orbit both nuclei more equally, forming a *covalent* bond. Covalent bonds are stronger than ionic bonds, and such minerals are far less soluble. Full covalent bonding occurs in compounds such as $O_2$ and $N_2$, and between the S atoms in pyrite [$FeS_2$] for example. Bonds between non-metals with similar electronegativities also bond covalently. The silica cation $Si^{4+}$ forms covalent bonds in tetrahedral coordination with $O^{2-}$ ions, giving silicate minerals like quartz a low solubility.

Oxygen (valence 2–) and many of the common ions of the non-metals ($C^{4+}$, $N^{5+}$, $Si^{8+}$, $P^{7+}$, $S^{6+}$; Fig. 1–4) have similar electronegativities, and form very stable, covalently-bonded anions — $CO_3^{2-}$, $NO_3^-$, $SiO_4^{4-}$, $PO_4^{3-}$ and $SO_4^{2-}$. Predominantly ionic bonding with common cations (e.g. $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$) gives the basic mineral groups discussed in Chapter 1. Nitrate compounds, like $KNO_3$ (saltpeter) are bonded by a single-charge ionic bond and so the nitrate salts are among the most soluble. Similarly, ionic bonding between $Ca^{2+}$ and $SO_4^{2-}$ or $CO_3^{2-}$ accounts for the relatively high solubility of gypsum and calcite.

Weak *van der Waals* forces exist between all atoms, and are unrelated to charge or electronegativity. Such forces hold together the sheets of phylosilicates (micas and clays), and cause the flocculation of colloids in high salinity solutions.

In water, we must consider one very important bond — the hydrogen bond, introduced in Chapter 1. This is the weak attractive force between polar $H_2O$ molecules, and which provides the loose tetrahedral structure of condensed water. Although the $H_2O$ molecule has no net positive or negative charge, its surface charge distribution is not uniform. Electrostatic attraction between the negative and positive ends of adjacent molecules provides the loose structure of water and rigid framework of ice.

Finally, anions and cations in solution experience a weak electrostatic attraction. Although similar to the ionic bond in minerals, it differs in that the anion and cation are separated by the surrounding hydration sheath of water molecules. Electrostatic bonding also occurs between ions and charged surfaces such as clays and solid organic matter.

## DISSOCIATION REACTIONS

A range of aqueous reactions involve the dissociation of ionic bonds and the formation and exchange of ions in solution. While often classified as acid-base reactions, they are more than this, ranging from simple acid dissociation reactions to mineral dissolution, ion hydration and formation of complex ions.

### *pH and dissociation of acids*

The most fundamental of all aqueous geochemical reactions is the dissociation of water:

$$H_2O \Leftrightarrow H^+ + OH^-$$
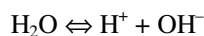
This reaction proceeds rapidly in both forward and reverse directions, such that in pure water at 25°C, the activity of $H^+$ and $OH^-$ are $10^{-7}$ (some 0.1 ppb for $H^+$). Note that while it is common practice to write geochemical reactions with free protons — $H^+$, they typically exist in the form $H_3O^+$. Changes in acidity affect the hydroxide activity through the dissociation constant for water:

$$K_{H_2O} = a_{H^+} \cdot a_{OH^-} = 10^{-14.0} @25° \, C$$

The pH scale for water changes with temperature. At 0°C $K_{H_2O} = 10^{-14.9}$ and the pH is 7.45, i.e. less water is dissociated. For water at 100°C, $K_{H_2O} = 10^{-13.0}$ and the pH is 6.5, indicating a higher activity for $H^+$ and for $OH^-$ due to greater dissociation of $H_2O$.

The acidity of water is the sum of the molalities of proton-donating species or acids at a given pH. Some of the major sources of acidity in waters include:

Carbonic acid — $H_2CO_3$ from dissolution of $CO_2$ in soils (oxidation of organics) or from geogenic sources including mantle and metamorphic $CO_2$ in tectonic areas.

Sulfuric acid — $H_2SO_4$ from the oxidation of sulfide minerals, $FeS_2$ in particular in mining areas, and from the oxidation of atmospheric $SO_2$ from industrial sources and coal-fired power plants.

Nitric acid — $HNO_3$ from $NO_x$ emissions from industrial, automotive and power generating sources.

Organic acids — the generation of heterogeneous humic and fulvic acids in soils as well as low molecular weight fatty acids such as acetic [$CH_3COOH$]

The principal acids in natural water and their dissociation constants are given in Table 2-1. Curves showing the distribution (relative concentration) of the acid and dissociation product for selected acids ($CH_2COOH$, $H_2CO_3$, $H_2S$ and $H_3BO_3$) are given in Fig. 2-3.

Table 2-1   Common acids in groundwater and their 1st dissociation constant, in order of increasing strength

| Acid | 1st dissociation constant, K | pH at 50% dissociated |
|---|---|---|
| Silicic acid – $H_4SiO_4$ | $K_{H_4SiO_4} = \dfrac{a_{H_3SiO_4^-} \cdot a_{H^+}}{a_{H_4SiO_4}} = 10^{-9.83}$ | 9.83 |
| Boric acid – $H_3BO_3$ | $K_{H_3BO_3} = \dfrac{a_{H_2BO_3^-} \cdot a_{H^+}}{a_{H_3BO_3}} = 10^{-9.24}$ | 9.24 |
| Hydrogen sulfide – $H_2S$ | $K_{H_2S} = \dfrac{a_{HS^-} \cdot a_{H^+}}{a_{H_2S}} = 10^{-6.99}$ | 6.99 |
| Carbonic acid – $H_2CO_3$ | $K_{H_2CO_3} = \dfrac{a_{HCO_3^-} \cdot a_{H^+}}{a_{H_2CO_3}} = 10^{-6.35}$ | 6.35 |
| Acetic acid – $CH_3COOH$ | $K_{CH_3COOH} = \dfrac{a_{CHCOO^-} \cdot a_{H+}}{a_{CH_3COOH}} = 10^{-4.74}$ | 4.74 |
| Humic acid – HA | $K_{HA} = \dfrac{a_{HA^-} \cdot a_{H+}}{a_{HA}} \approx 10^{-2}$ to $10^{-4}$ | ~ 2 to 4 |
| Phosphoric acid – $H_3PO_4$ | $K_{H_3PO_4} = \dfrac{a_{H_2PO_4^{2-}} \cdot a_{H+}}{a_{H_3PO_4^o}} = 10^{-2.15}$ | 2.15 |
| Bisulfate – $HSO_4^-$ | $K_{HSO_4^-} = \dfrac{a_{SO_4^{2-}} \cdot a_{H+}}{a_{HSO_4^-}} = 10^{-1.99}$ | 1.99 |

Note that $HNO_3$, $HCl$ and $H_2SO_4$ are strong acids, and dissociate to nitrate — $NO_3^-$, chloride — $Cl^-$ and bisulfate — $HSO_4^-$, respectively, below pH 0 (where $a_{H^+} > 1$). Bisulfate dissociates to $SO_4^{2-}$ above pH 2. Bicarbonate — $HCO_3^-$, generated by the dissociation of carbonic acid, becomes the dominant dissolved carbonate species above pH 6.35. At higher pH values (>8.4), bicarbonate acts as an acid by dissociating to form dissolved carbonate $CO_3^{2-}$ ($K_{HCO_3-} = 10^{-10.33}$).



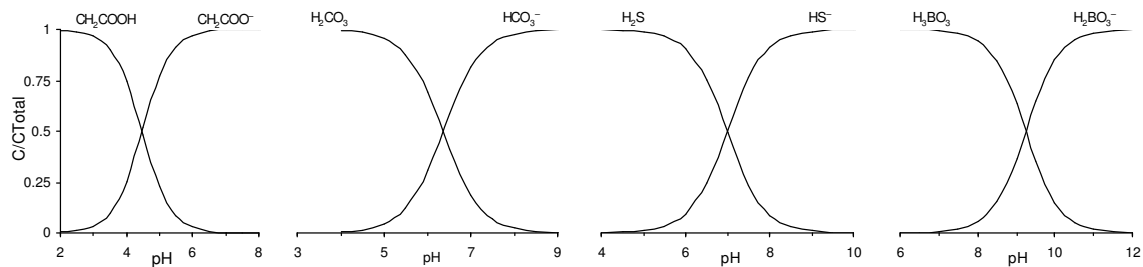Fig. 2-3   Relative concentration curves for the dissociation of common weak acids in groundwater.

Phosphoric acid is found only at low concentrations in natural waters, and so contributes little to acidity. Silicic and boric acids are also present in generally low concentrations. As their first dissociation constants are very low, they are not dissociated in most natural waters. Thus, in the pH range of 6 to 8 found in most
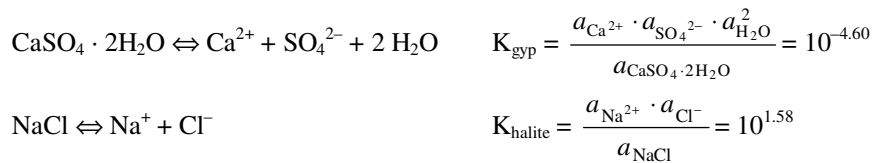
natural waters, only bicarbonate $HCO_3^-$ will accept or donate a proton. This makes it an important contributor to alkalinity and the natural buffering of pH.

### *Dissociation of salts*

Salts are the reaction products from the mixture of acids and bases such as sulfuric acid [$H_2SO_4$] and calcium hydroxide — portlandite [$Ca(OH)_2$] which produce a $Ca^{2+}$ - $SO_4^{2-}$ solution which can precipitate gypsum [$CaSO_4 \cdot 2H_2O$]. While seldom in geochemical settings do such acid-base mixtures occur directly, their salts are very common. Dissociation of the salts of strong acids (sulfuric, hydrochloric, nitric acid) and bases (sodium and calcium hydroxide) do not usually affect pH, but they do contribute to salinity. Moreover, such salts have high solubility.

The highly soluble salts, discussed in chapter 1, are the evaporite minerals, including gypsum [$CaSO_4 \cdot 2H_2O$], halite [$NaCl$] and sylvite [$KCl$]. They are commonly found in sedimentary rock sequences formed in restricted marine basins with strong evaporation. They are also common in soils from arid regions, where at least seasonally, dry conditions provoke their precipitation from saline pore waters. Under more extreme conditions, nitrate salts, like sodium nitrate [$NaNO_3$] can form, such as were mined in the Atacama desert in the Andean rain shadow of Chile.

The dissociation reactions of the major salts are simple:

$$CaSO_4 \cdot 2H_2O \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2\,H_2O \qquad K_{gyp} = \frac{a_{Ca^{2+}} \cdot a_{SO_4^{2-}} \cdot a_{H_2O}^2}{a_{CaSO_4 \cdot 2H_2O}} = 10^{-4.60}$$

$$NaCl \Leftrightarrow Na^+ + Cl^- \qquad K_{halite} = \frac{a_{Na^{2+}} \cdot a_{Cl^-}}{a_{NaCl}} = 10^{1.58}$$

From these reactions, we see that there is no effect on pH for salts of the strong bases (alkalis and alkali earth cations). For others, subsequent reactions with water including ion hydration and hydrolysis begin to have an effect on the activity of water and on pH.

### *Ion hydration*

The bipolar nature of water and the ease with which the $H_2O$ molecule can dissociate into hydroxide [$OH^-$] and hydrogen [$H^+$] ions make water a very powerful solvent. At the basis of mineral dissolution reactions is the capacity for water to coordinate around and react with ions, thereby greatly increasing their solubility. This is ion hydration, a fundamental reaction in water. Dissolution reactions involve the uptake of ions into solution by the hydration of the component ions. Orientation of polar $H_2O$ molecules around the ion by reduces its ability to react with an oppositely charged ion and reform a solid mineral phase, and so enhances solubility. The dissolution of a salt, say fluorite — $CaF_2$, is a good example:

$$CaF_2 \Leftrightarrow Ca^{2+} + 2F^-$$
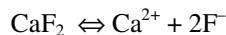
In writing this reaction for the dissolution of fluorite the hydration role played by water is not explicitly written, but the hydration reactions and their aqueous complex can be approximated by:
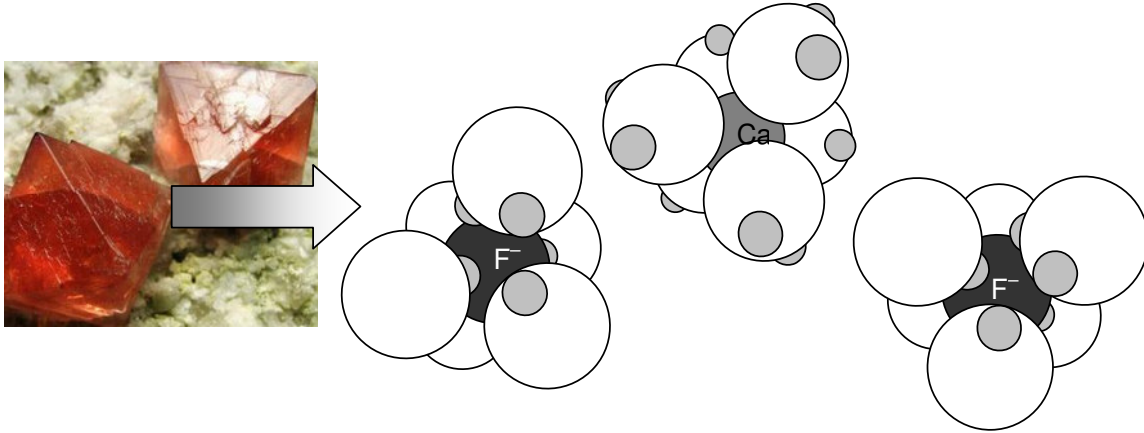
$$Ca^{2+} + 6H_2O \rightarrow Ca(H_2O)_6^{2+}$$
$$F^- + 6H_2O \rightarrow F(H_2O)_6^-$$
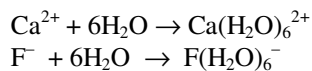
Fig. 2-4   Dissolution of fluorite [$CaF_2$] and hydration of $Ca^{2+}$ and $F^-$.

The charge of these ions is felt beyond this hydration sheath of water molecules, such that there is a loose orientation of $H_2O$ molecules around these ions that decreases with distance from the ion. The number of water molecules fixed in a hydration sheath depends on the valence of the ion and its ionic radius. The extent of ion hydration is proportional to the ionic potential or charge to radius ratio — z/r. Smaller ions like $Li^+$ or $Be^{2+}$ have a higher net surface charge than say $K^+$ and $Ca^{2+}$, and so have more coordinated water molecules. This leads to the relationship where smaller ions have a larger hydrated radius than larger ions, shown in Table 2-2.

Table 2-2   Crystallographic ($R_c$) and hydrated ($R_h$) radii (in angstrom units, Å = $10^{-10}$ m = 100 pm) for the alkalis and alkaline-earth elements,   (Shannon, 1976; Parkhurst, 1990). The radius of $H_2O$ is 1.4 Å

| Element | $R_c$ | $R_h$ | Element | $R_c$ | $R_h$ |
|---------|-------|-------|---------|-------|-------|
| $H^+$   | —     | 4.5   | $Be^{2+}$ | 0.31 | 4.0 |
| $Li^+$  | 0.94  | 3.0   | $Mg^{2+}$ | 0.72 | 4.0 |
| $Na^+$  | 1.17  | 2.0   | $Ca^{2+}$ | 1.00 | 3.0 |
| $K^+$   | 1.49  | 1.8   | $Sr^{2+}$ | 1.26 | 2.5 |
| $Rb^+$  | 1.63  | 1.3   | $Ba^{2+}$ | 1.42 | 2.5 |
| $Cs^+$  | 1.86  | 1.3   | $Ra^{2+}$ | 1.48 | 2.5 |

A consequence of hydration or the "structuring" of water around ions is that the number of free water molecules in the solution is reduced. In highly saline solutions such as brines, the amount of structured water can approach and even exceed the amount of free water. This reduces the activity of free water for participation in geochemical reactions, with implications for the state of saturation of minerals. This also affects the isotopic composition of the free water, which becomes depleted in $^{18}O$ and $^2H$, as these heavier isotopes are selectively partitioned into the hydration sheaths (Gonfiantini, 1965).

### *Ion hydrolysis*

When the surface charge is extremely high, as in the case of trivalent $Al^{3+}$ or $Fe^{3+}$, the strong positive charge will force the hydrated ion to shed one or more $H^+$ ions from its hydration sheath into the bulk solution. The result is a complex with hydroxide — $OH^-$, generating a new ion with lower net charge. The consequence of hydrolysis of metals dissolved in water is a decrease in pH, as hydrogen ions are expelled into solution. At the same time, the pH of the solution will affect the stability of metal hydroxide complexes in solution. The following series of hydrolysis reactions for ferric iron $Fe^{3+}$ are a good example, which through the common variable of pH, produces the ferric iron speciation diagram of Fig. 2-5.

$$Fe^{3+} + H_2O \Leftrightarrow Fe(OH)^{2+} + H^+ \qquad K = \frac{a_{Fe(OH)^{2+}} \cdot a_{H^+}}{a_{Fe^{3+}}} = 10^{-2.19} \qquad \frac{a_{Fe(OH)^{2+}}}{a_{Fe^{3+}}} = 1 \text{ @ pH 2.19}$$

$$Fe(OH)^{2+} + H_2O \Leftrightarrow Fe(OH)_2^+ + H^+ \qquad K = \frac{a_{Fe(OH)_2^+} \cdot a_{H^+}}{a_{Fe(OH)^{2+}}} = 10^{-3.48} \qquad \frac{a_{Fe(OH)_2^+}}{a_{Fe(OH)^{2+}}} = 1 \text{ @ pH 3.48}$$

$$Fe(OH)_2^+ + H_2O \Leftrightarrow Fe(OH)_3^\circ + H^+ \qquad K = \frac{a_{Fe(OH)_3^o} \cdot a_{H^+}}{a_{Fe(OH)_2^+}} = 10^{-6.89} \qquad \frac{a_{Fe(OH)_3^o}}{a_{Fe(OH)_2^+}} = 1 \text{ @ pH 6.89}$$

$$Fe(OH)_3^\circ + H_2O \Leftrightarrow Fe(OH)_4^- + H^+ \qquad K = \frac{a_{Fe(OH)_4^-} \cdot a_{H^+}}{a_{Fe(OH)_3^o}} = 10^{-9.04} \qquad \frac{a_{Fe(OH)_4^-}}{a_{Fe(OH)_3^o}} = 1 \text{ @ pH 9.04}$$

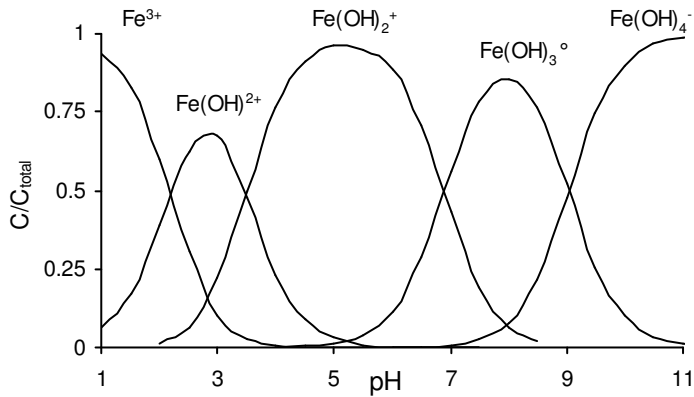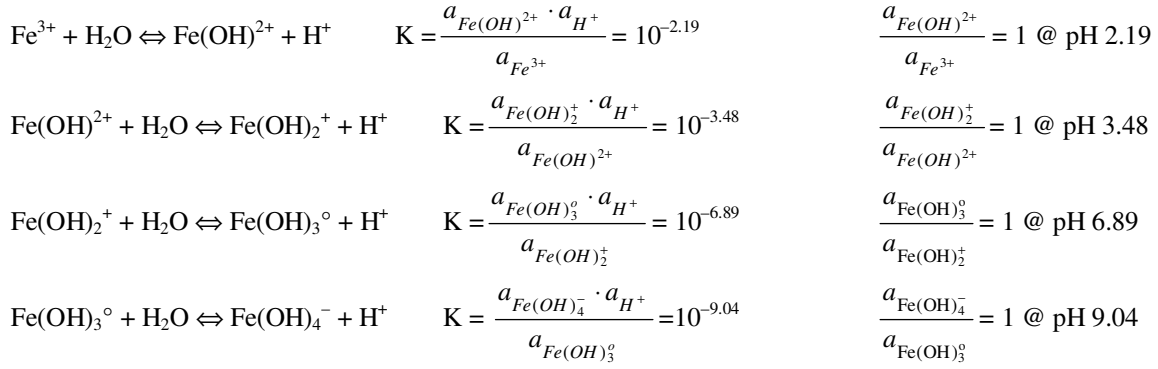

Fig. 2-5  The distribution of iron hydroxide species with pH, given as the concentration of each species over the total dissolved iron concentration, $C/C_{total}$. Only at very low pH (high $H^+$ activity and low $OH^-$ activity) does unhydroxylated $Fe^{3+}$ exist in solution. While it will be hydrated, it retains its 3+ charge. Note that this graph shows only relative concentrations of ferric iron species in solution, not total concentration, which is discussed in a later chapter. Note that $Fe(OH)_3^\circ$ is a neutral (uncharged) species.

Aluminum, the third most abundant element in the Earth's crust, is another good example of ion hydrolysis, and the effect on pH. Like ferric iron, $Al^{3+}$ has a high surface charge, which allows it to repel $H^+$ ions from its hydration sheath. This generates a series of aluminum hydroxide species that range from uncomplexed (but still hydrated) $Al^{3+}$ to aluminum that is coordinated with four hydroxide ions, becoming an anion – $Al(OH)_4^-$ (Fig. 2-6).
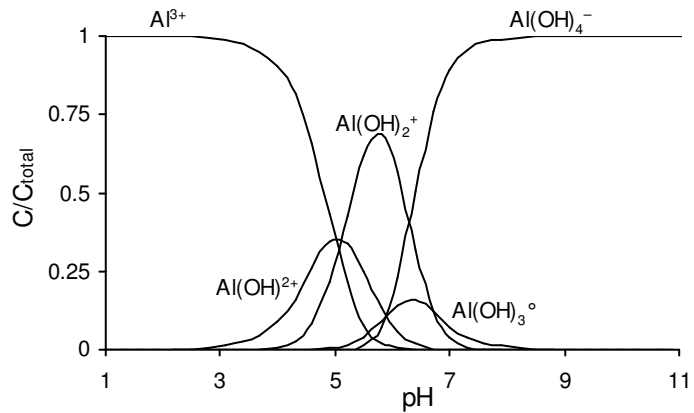


Fig. 2-6  The distribution of aluminum hydroxide species according to pH, given as concentration relative to total dissolved Al.

For ions with very high surface charge, hydrolysis is even stronger. Silica is an example. As $Si^{4+}$, silicon (the element) readily coordinates with four water molecules, which all shed their hydrogen ions to form the stable form of dissolved silica (silicon coordinated with oxygen) — $H_4SiO_4°$.  Note the difference in expressing this species, which could as easily be written as $Si(OH)_4$. However, as seen in Fig. 2-7, even at low pH where $H^+$ ions are abundant, they are still rejected from the hydroxyls coordinated with $Si^{4+}$ and so species such as $Si(OH)_3^+$ simply don't exist. Sulfate is an even more extreme example. Oxidized sulfur, as $S^{6+}$ (a very small ion) also coordinates with four water molecules, but all $H^+$ ions are readily ejected into the bulk solution, leaving the soluble anion $SO_4^{2-}$. Only when the $H^+$ activity is as high as 0.01 (pH 2) does a first association product, $HSO_4^-$, appear. However, this is far from actually producing a cation such as the imaginary species or $HSO_3^+$ or $HS(OH)_4^+$. The strong positive surface charge of the $S^{6+}$ ion is too great.
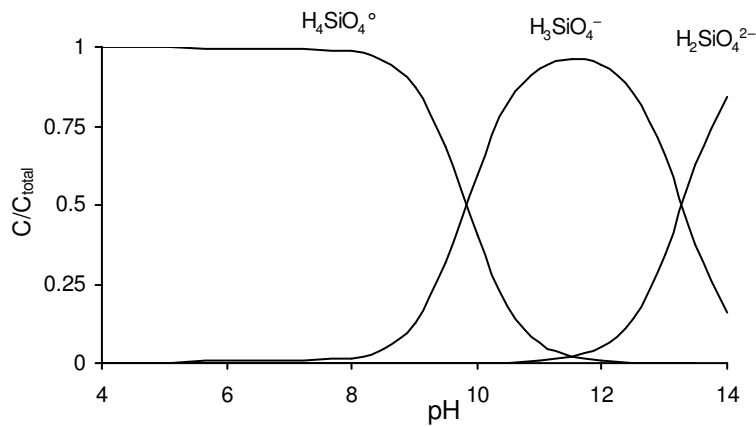
Fig. 2-7  The silicic acid dissociation products as a function of pH. Note that silica in solution is always anionic, due to the high surface charge of the $Si^{4+}$ ion which expels even the second $H^+$ ion from some of its hydration waters. For the pH range of most natural waters, the unionized species — $H_4SiO_4°$ is the dominant dissolved silica species and maintains a relatively low dissolved concentration. However, the dominance of the anion $H_3SiO_4^-$ at high pH greatly increases the solubility of silica in alkaline waters.

With this understanding of hydrolysis, we can predict the occurrence of hydroxide species for elements with low electromotive potential from the left side of the periodic table. Hydrolysis with the alkaline earth elements like $Mg^{2+}$ and $Ca^{2+}$ does not occur until hydroxide activities are very high, at pH greater than 10. For the alkalis — $Na^+$ and $K^+$, their hydroxides caustic soda [NaOH] and caustic potash [KOH] dissociate near pH 14.
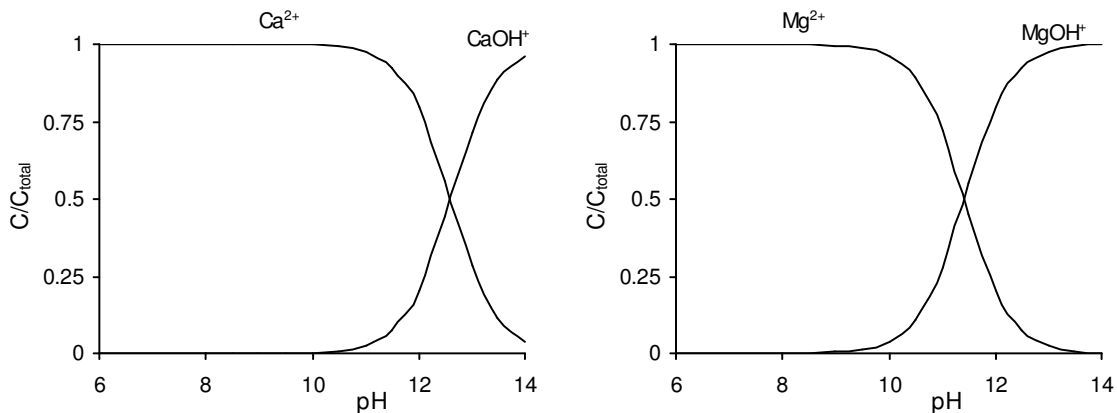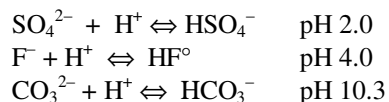
Fig. 2-8  Hydrolysis of $Ca^{2+}$ and $Mg^{2+}$ occurs only at high pH. Although hydrated with six water molecules surrounding these ions in solution, they do not hydrolyze except under very alkaline conditions. Note that $Mg^{2+}$ has a smaller diameter and higher surface charge than $Ca^{2+}$ and so can hydrolyze at a lower pH.
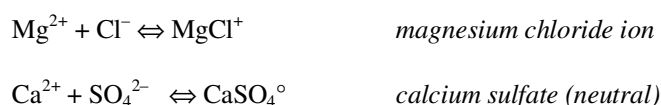
Anion hydrolysis is the reverse of cation hydrolysis, and acts to expel hydroxyls [OH⁻] from their hydration sheath into the bulk solution, retaining only a proton [H⁺]. Anion hydrolysis is common for multivalent ions, but is rarely observed for common monovalent ions such as Cl⁻ or NO₃⁻, due to their very low ionic potentials. It does occur with F⁻ due to its small crystallographic radius which gives it a high ionic potential. Common anion hydrolysis reactions, and the pH at their point of equivalence, include:

$$SO_4^{2-} + H^+ \Leftrightarrow HSO_4^- \qquad pH\ 2.0$$
$$F^- + H^+ \Leftrightarrow HF° \qquad pH\ 4.0$$
$$CO_3^{2-} + H^+ \Leftrightarrow HCO_3^- \qquad pH\ 10.3$$

In fact, these are no more than acid dissociation reactions written in reverse, which underlines the point that ion hydrolysis is essentially another perspective of acid-base reactions and the dissociation of water. The importance of pH in geochemistry cannot be overemphasized. It affects virtually all reactions and ion solubilities.

## Complexation reactions

Reaction between solutes in solution should also be considered. In this case, dissolved ions and complexes can react to form new complexes:

$$Mg^{2+} + Cl^- \Leftrightarrow MgCl^+ \qquad\qquad \textit{magnesium chloride ion}$$

$$Ca^{2+} + SO_4^{2-} \Leftrightarrow CaSO_4° \qquad\qquad \textit{calcium sulfate (neutral)}$$

In such reactions, the complexes formed are discrete species dissolved in water, not a solid phase, and can experience some degree of hydration and /or hydrolysis, depending on ionic potential.

## Incongruent dissolution

The final group of reactions to be introduced is that where minerals dissolve incongruently, with solid and dissolved reaction products. The mineral dissolution reactions presented above involve the complete dissolution of the solid phase to produce only aqueous components. However, some dissolution reactions involve the precipitation of complementary mineral or amorphous solids at the dissolution site. Weathering of silicate minerals generally occurs incongruently. For example:

Feldspar weathering involves the dissolution of a primary silicate and the formation of a secondary clay mineral, such as the dissolution of plagioclase (anorthite in this case) and precipitation of kaolinite clay on the weathered surfaces of the primary feldspar. Like most mineral weathering reactions, it is acid consuming resulting in higher a pH.

$$CaAl_2Si_2O_{8\ anorthite} + H_2O + 2H^+ \rightarrow Ca^{2+} + Al_2Si_2O_5(OH)_{4\ kaolinite}$$
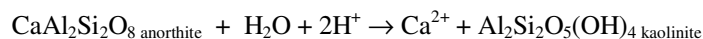
Clay minerals such as kaolinite can be further leached of their silica, producing more highly insoluble aluminum oxide and dissolved silica:

$$Al_2Si_2O_5(OH)_{4\ kaolinite} + 5H_2O \rightarrow 2Al(OH)_{3\ gibbsite} + 2H_4SiO_4°$$
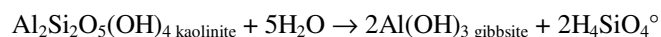
Another common example involves the dissolution of dolomite by Ca²⁺-bearing waters, resulting in the precipitation of calcite:

$$Ca^{2+} + CaMg(CO_3)_{2\ dolomite} \rightarrow Mg^{2+} + 2CaCO_{3\ calcite}$$
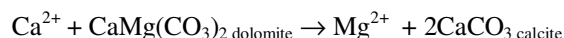
### Balancing dissociation reactions

Any reaction can be written as long as it balances both atoms and charges on both sides. Whether the reaction will actually take place is another matter that depends on the relative stability of the products 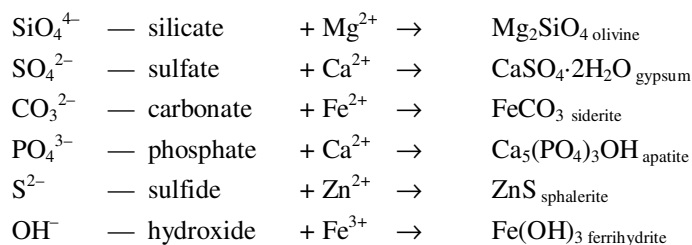as compared with other possible phases. Thus, the thermodynamic likelihood for a reaction to take place is another question, which is looked at later in this chapter.

Writing a geochemical reaction such as for mineral dissolution or precipitation begins with recognition of the basic components and their charge or valence. Most rock-forming minerals and compounds are composed of varying numbers of cations and anions, with or without water (as $H_2O$ or $OH^-$). The anions define the class of mineral (recall from Chapter 1), and the cations define the mineral within that class:

$$SiO_4{}^{4-} \;—\; \text{silicate} \quad + Mg^{2+} \;\rightarrow\; Mg_2SiO_4{}_{\text{ olivine}}$$
$$SO_4{}^{2-} \;—\; \text{sulfate} \quad + Ca^{2+} \;\rightarrow\; CaSO_4{\cdot}2H_2O{}_{\text{ gypsum}}$$
$$CO_3{}^{2-} \;—\; \text{carbonate} \quad + Fe^{2+} \;\rightarrow\; FeCO_3{}_{\text{ siderite}}$$
$$PO_4{}^{3-} \;—\; \text{phosphate} \quad + Ca^{2+} \;\rightarrow\; Ca_5(PO_4)_3OH{}_{\text{ apatite}}$$
$$S^{2-} \;—\; \text{sulfide} \quad + Zn^{2+} \;\rightarrow\; ZnS{}_{\text{ sphalerite}}$$
$$OH^- \;—\; \text{hydroxide} \quad + Fe^{3+} \;\rightarrow\; Fe(OH)_3{}_{\text{ ferrihydrite}}$$

In the case of gypsum and apatite, water and hydroxide are involved structurally in forming these minerals. Care must be taken to consider the appropriate redox state of the ions involved, as these are not necessarily apparent from the mineral formula. Iron is a good example, as it can be present as either ferrous — $Fe^{2+}$ or ferric — $Fe^{3+}$ iron. Accounting for charges within the anion component is required, and so for ferrihydrite, the three hydroxides give a net negative charge of 3–, and so iron must be $Fe^{3+}$.

The simplest approach in balancing a geochemical equation in which no elements exchange electrons (i.e. no change in redox conditions) is to begin by placing the reactants and products on the left and right sides. In straight dissolution equation, the products may not yet be established and so the right side is blank. If the product is a secondary mineral phase, this should be written on the right side.

The next step is to indicate the cations and anions liberated by the reaction, either those not present in the product, or those formed by dissociation of the reacting mineral. With major cations and anions accounted for, oxygen ($O^{2-}$) or hydrogen ($H^+$) are accounted for by addition of $H_2O$ or $H^+$ to either side as appropriate. Finally, check that all elements and all charges are equal on both sides. If the reaction is charge and mass balanced, then it is correct.

Example 2-1   Balancing dissociation reactions

---

*Write a reaction for the dissolution of gypsum in pure water.*

Writing the reactant:
$$CaSO_4{\cdot}2H_2O \;\rightarrow$$
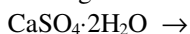
Accounting for cations and anions:
$$CaSO_4{\cdot}2H_2O \;\rightarrow\; Ca^{2+} + SO_4{}^{2-}$$
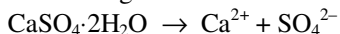
Adding the structural water of gypsum released by dissolution completes the reaction:
$$CaSO_4{\cdot}2H_2O \;\rightarrow\; Ca^{2+} + SO_4{}^{2-} + 2H_2O$$

Both mass and charge are balanced between the left and right sides. Note that this reaction is pH neutral, which is typical of salt dissolution reactions.

*Balance a reaction for the alteration of anorthite to kaolinite.*

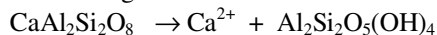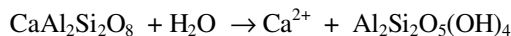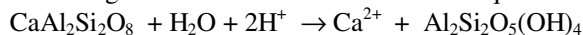Reactant: $CaAl_2Si_2O_{8\ anorthite} \rightarrow$ Product: $Al_2Si_2O_5(OH)_{4\ kaolinite}$
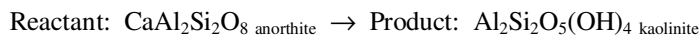
Accounting for cations and anions liberated in the reaction:
$$CaAl_2Si_2O_8 \rightarrow Ca^{2+} + Al_2Si_2O_5(OH)_4$$

Balancing oxygen using water. Here the left side requires one $H_2O$ to match the 9 oxygen atoms in kaolinite:
$$CaAl_2Si_2O_8 + H_2O \rightarrow Ca^{2+} + Al_2Si_2O_5(OH)_4$$

Balancing $H^+$. An additional 2 $H^+$ ions are required on the left:
$$CaAl_2Si_2O_8 + H_2O + 2H^+ \rightarrow Ca^{2+} + Al_2Si_2O_5(OH)_4$$

A quick check on charge balance shows that each side has 2+, and mass is equal on both sides. The equation is balanced. Here we find that this reaction is acid-consuming, and will cause an increase in pH, typical of weathering reactions.

*Write a reaction for the dissolution of ferrihydrite with carbonic acid.*
Reactants: $Fe(OH)_3 + H_2CO_3 \rightarrow$

Accounting for cations and anions: $Fe(OH)_3 + H_2CO_3 \rightarrow Fe(OH)_2^+ + HCO_3^-$

Balance oxygen with $H_2O$: $Fe(OH)_3 + H_2CO_3 \rightarrow Fe(OH)_2^+ + HCO_3^- + H_2O$

No $H^+$ needed: $Fe(OH)_3 + H_2CO_3 \rightarrow Fe(OH)_2^+ + HCO_3^- + H_2O$
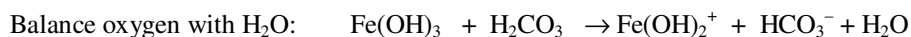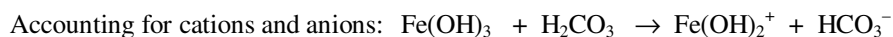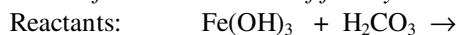
The charges balance on both sides, and so the equation checks out.

---

### Equilibrium and kinetic reaction

Much of the study of geochemistry has to do with determining the state of disequilibrium for aqueous reactions. Note that the above reactions are written with a double arrow $\Leftrightarrow$. This signifies that the reaction is proceeding in both directions at equal rates. This is the condition of equilibrium, and so there is no net flux of mass from one side of the equation to the other. A reaction written with a one-way arrow $\rightarrow$ signifies a kinetic reaction, which is proceeding preferentially in one direction.

If a mineral like halite is placed in pure water, it will begin to dissolve. Initially there is a net flux from the mineral to the solution. At the same time, $Na^+$ and $Cl^-$ ions in solution can combine and re-precipitate on the mineral surface. The rate of this reverse reaction depends on the $Na^+$ and $Cl^-$ concentrations in solution, and will accelerate as dissolution proceeds. Accordingly, the buildup in concentration of $Na^+$ and $Cl^-$ will slow down over time (Fig. 2-9). At the point of equilibrium, both forward and reverse reactions will have the same rate and there will be no net mineral dissolution. Although there is no net flux during equilibrium reaction, both dissolution and re-precipitation will continue at the mineral surface. This is often referred to as an aging process, which reduces the surface free energy by increasing crystal size and removing lattice imperfections.

Rates of reactions that involve changes of phase such as mineral precipitation can be impeded by the rates of diffusion between the reaction surface and the bulk reservoir. In groundwaters where the distances between particles or fracture surfaces are short, diffusion through the bulk solution is fast and won't impede rates of reaction on the solid surfaces. However, diffusion of $CO_2$, for example out of a lake into the open atmosphere may be much slower than the rates of reaction producing it in the water column, and so the lake

water will be over-pressured and out of equilibrium with the adjacent atmosphere. For this reason, equilibrium between reacting phases may not be readily established.  Purely aqueous reactions, such as the hydration of $CO_2$ and dissociation of carbonic acid are not constrained by an interface, and so achieve equilibrium almost immediately.
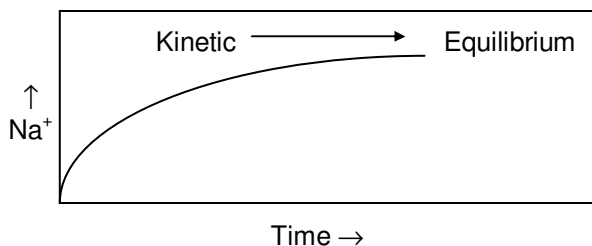


Fig. 2-9   Kinetic and equilibrium reaction, shown schematically by the rate of increase of aqueous $Na^+$ as halite dissolves.

## SOLUBILITY, SOLUTES AND SPECIATION

Calculations of mineral solubility, solute concentrations and the forms or speciation of these solutes are based on equilibrium thermodynamics. Natural geochemical systems are dynamic and evolving, and hence are seldom in complete equilibrium. Nonetheless, the state of equilibrium provides a datum to determine the direction that a geochemical system is moving, according to the law of mass action described above. If, for example, the concentrations of $Ca^+$ and $SO_4^{2-}$ in groundwater are lower than at the point of gypsum [$CaSO_4·2H_2O$] saturation, gypsum (if present) will dissolved until equilibrium is reached. Similarly, if the partial pressure of a dissolved gas is greater than its atmospheric partial pressure, it will degas until the equilibrium partial pressure is reached.

To evaluate the state of equilibrium for a given reaction, the approach is based on the activities — *a* of reactants and products, and the equilibrium reaction constant — K. Activities of geochemical species are essentially their thermodynamic concentration, i.e. the effective concentration that defines its ability to participate in a reaction. This differs from its analytical concentration which is a measure of the total concentration of that species in solution. The total concentration is invariably greater than its activity.

### *Ion activity and the activity coefficient in aqueous solutions*

The molality of a given ion, $m_i$, is its concentration, expressed in mol/kg. This can differ from its analytical or input concentration, which would include the concentrations of any complex ions involving that ion. The formation of complex ions is further discussed below. In aqueous solutions, ions interact electrostatically with other oppositely-charged ions in solution according to their chemical potential, allowing them to complex and to form minerals. The chemical potential for reaction for a given ion increases with its concentration. However, at the same time, its chemical potential decreases as the density of other charges in solution goes up, due to increased electrostatic interaction with the ion of interest. The increase in charge density is the *ionic strength — I* of the solution. It is a bit like finding a friend on a ski hill. The bigger your group of friends, the more likely you are of finding one. However, as the ski hill gets crowded, the likelihood of finding one of your friends in the growing crowd is diminished. This effect of concentration (number of friends you might find) and ionic strength (crowd size to find them in) is to decrease an ion's effective concentration in solution and obliges us to use ion *activity — $a_i$*, rather than molality, $m_i$, when calculating ion interactions and thermodynamic reactions. An ion activity can be thought of as its effective or thermodynamic concentration, which in most solutions is somewhat less than its total concentration. In fact, ion activity is a scalar variable and so is unit-less. It is related to solute concentrations (molality, mol/kg) through the activity coefficient $\gamma$, which has units of inverse concentration, or kg/mol.

$$a_i = m_i \cdot \gamma_i \quad [\text{mol/kg} \cdot \text{kg/mol}]$$

In low salinity water, $\gamma_i$ is close to 1 and so ion activities have the same numeric value as their concentration. However, as ionic strength increases, the activity coefficient decreases and the ion activity become a fraction of the ion concentration. The values for $\gamma$ and $a$ decrease not only with increasing salinity, they are also lower for ions with higher charge. Some points on activity coefficients:

- $\gamma \approx 1$ for ions in fresh waters,
- $\gamma$ decreases with increasing salinity
- in seawater, $\gamma$ is about 0.8 for mono-valent ions and about 0.2 for divalent ions.
- $\gamma = 1$ for uncharged species (e.g. $H_4SiO_4°$ or $H_2CO_3°$) which do not contribute to ionic strength.
- $\gamma_{H_2O} < 1$ for waters with high ionic strength.

The activity of an ion is attenuated by electrostatic interactions with other ions, and so activity coefficients become lower in higher salinity waters. Thus, $\gamma$ is a function of the *ionic strength — I* of the solution, calculated from the sum of the molalities of all major ions in solution times the square of their valence:

$$I = \tfrac{1}{2} \sum m_i z_i^2$$

where:  $z$ is the charge of the ith ion
         $m$ is the molality of the ith ion

Example 2-2   Ionic strength for different 1 molal salt solutions

---

*What is the ionic strength of a 1m solution of:*

NaCl
$$\begin{aligned} I &= \tfrac{1}{2} (m_{Na^+} z_{Na^+}^2 + m_{Cl^-} z_{Cl^-}^2) \\ &= \tfrac{1}{2} (1 \times 1^2 + 1 \times 1^2) \\ &= 1 \end{aligned}$$

$Na_2SO_4$
$$\begin{aligned} I &= \tfrac{1}{2} (m_{Na^+} z_{Na^+}^2 + m_{SO_4^{2-}} z_{SO_4^{2-}}^2) \\ &= \tfrac{1}{2} (2 \times 1^2 + 1 \times 2^2) \\ &= 3 \end{aligned}$$

*What is the ionic strength of the following groundwater:*

| | | | |
|---|---|---|---|
| $Ca^{2+}$ — 86 ppm | | $HCO_3^-$ — 280 ppm | |
| $Mg^{2+}$ — 33 | | $SO_4^{2-}$ — 120 | |
| $Na^+$ — 24 | | $Cl^-$ — 37 | |
| $K^+$ — 3.2 | | | |

$$\begin{aligned} I &= \tfrac{1}{2} (4m_{Ca^{2+}} + 4m_{Mg^{2+}} + m_{Na^+} + m_{K^+} + m_{HCO_3^-} + 4m_{SO_4^{2-}} + m_{Cl^-}) \\ &= \tfrac{1}{2} (4[86/40.1/1000] + 4[33/24.3/1000] + \dots) \\ &= 0.013 \end{aligned}$$

---

The activity coefficient $\gamma$ is calculated with the Debye-Hückel equation, which relates $\gamma$ to $z$ and $I$. The form of the Debye-Hückel equation depends on the salinity of the water. For fresh waters ($I < 0.01$) at temperatures up to about 50°C, the simplified form is very accurate:

$$\log \gamma_i = -0.5 \, z_i^2 \sqrt{I} \qquad\qquad \text{simplified Debye-Hückel equation}$$

The Debye-Hückel model of an infinitely small charge interacting in solution breaks down in higher salinity waters, ($I > 0.01$ or $>\sim 1000$ mg/L TDS), and the hydrated radius of the ion, å (in angstrom units, $10^{-8}$ cm) must be taken into account. This effect is taken into account by the extended Debye-Hückel equation including the Davies (1962) constant ($0.3I$), which is valid for solutions up to ionic strength of about 1 (i.e. greater than seawater, $I = 0.5$):

$$\log \gamma_i = \frac{-0.5\, z_i^2\, \sqrt{I}}{1 + 0.33\,\mathring{a}_i\, \sqrt{I}} + 0.3I$$

Values for the hydrated diameter of the common ions are:

$$\mathring{a} = 2.5 \;—\; NH_4^+$$
$$3.5 \;—\; K^+, Cl^-$$
$$4.0 \;—\; Na^+$$
$$5.0 \;—\; Ca^{2+}, SO_4^{2-}, Sr^{2+}, Ba^{2+}$$
$$5.5 \;—\; Mg,^{2+}, HCO_3^-, CO_3^{2-}$$

Refinements of the Davies equation, including ion-specific and temperature-dependent constants have been made (see Freeze and Cherry, 1979; Drever, 1997) and are incorporated in most computer codes for treating geochemical data (discussed below). Certain geochemical programs also handle hypersaline brines ($I > 1$), using equations that account for complicated ion interactions and reduced activity of water (Pitzer, 1987).
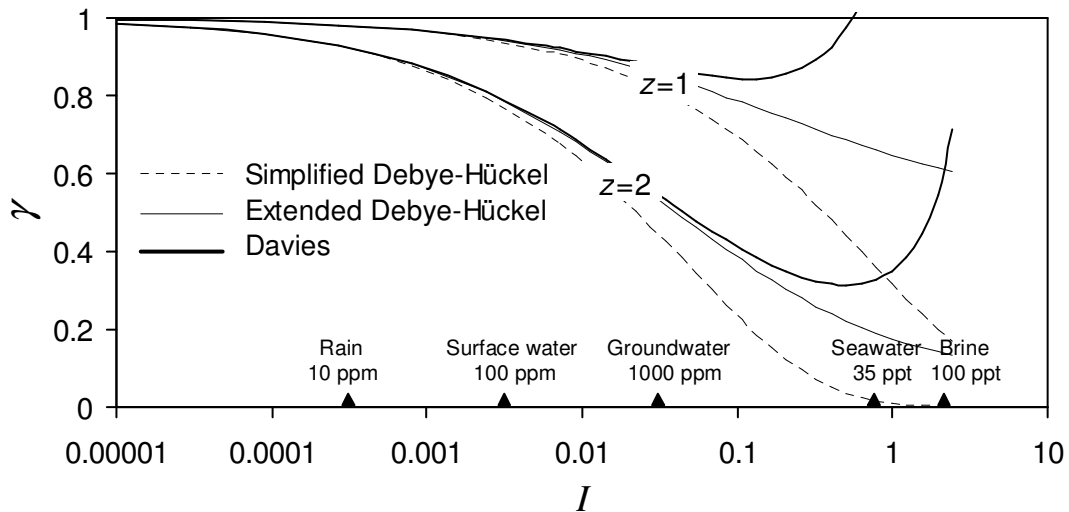


Fig. 2-10    Activity coefficient γ for monovalent ($z=1$) and divalent ($z=2$) ions, as a function of ionic strength. The simplified Debye-Hückel model is valid to $I \sim 0.05$, which includes most groundwaters up to a TDS of about 2000 ppm. Higher ionic strength waters are more accurately modeled using the extended Debye-Hückel, with the Davies coefficient, up to the salinity of brine ($I > 1$). The extended Debye-Hückel model requires the hydrated ionic radius, å, which in this graph was set at 5 ($Ca^{2+}$, $SO_4^{2-}$).

### *Activity of water and minerals*

Thermodynamic convention holds that the activity of solids and liquids are based on mole fraction, rather than concentration. Accordingly, pure mineral phases, such as pure calcite [$CaCO_3$] would have an activity

of 1 in thermodynamic calculations. However, substitution of ions occurs during crystal growth, producing mixtures such as strontium Sr replacing Ca in calcite. The resulting impure mineral will have an activity that is directly proportional to its molar percent of the solid phase. For example, if $SrCO_3$ represented 5% of the total calcite mineral, then the activity of calcite— $a_{CaCO_3}$, would be 0.95 rather than 1. The mole fraction for minerals and liquids is then the counterpart to the activity coefficient for solutes. In most mineral solubility calculations, only pure mineral phases are considered and so mineral activities are accepted to be 1.

Pure water itself has an activity of 1 (although its molality, $m_{H_2O}$ = 55.6 mol/kg, determined by dividing 1000 g by its gfw of 18). However, the activity of water also decreases with increased salinity due to the partitioning of water molecules from the open solution into ion hydration sheaths. In seawater, for example, $a_{H_2O}$ = 0.98, but drops closer to 0.8 in concentrated brines. Similarly, the activity of water decreases with increasing salinity.

### Activities in brines

The activities of solutes and of water in solutions of high ionic strength experience reversals that affect the solubilities of minerals and the formation of complex ions. In Fig. 2-10, the activity coefficients for monovalent and divalent ions reach minimum values at ion strength values near that of seawater. With increasing $I$, activity coefficients begin to increase, and within the range of brine, become greater than 1. In conjunction with this reversal is the enhancement of ion-ion interactions including not just binary interactions but ternary interactions as well. This leads to the creation of additional complex ions in the solution and a reduction in the activity of uncomplexed species involved in mineral precipitation reactions.

Predicting the solubility of minerals and stability of aqueous complexes becomes far more complicated than for the low-salinity systems discussed above. Ion interactions in brines have been successfully modeled by calculating excesses in Gibbs free energy, according to Pitzer (1980, 1987). Pitzer equations are incorporated into several computer codes for evaluating speciation and mineral solubilities in brines, discussed below.

### Equilibrium reaction constant K

The Law of Mass Action, introduced at the outset of this chapter, establishes that the activities of reactants and products in an equilibrium reaction are defined by a thermodynamic reaction constant, K, where:

$$K = \frac{activity\ of\ products}{activity\ of\ reactants}$$

For example, consider (i) a generic reaction where b moles of B and c moles of C react to form d moles of D and e moles of E, and (ii) the dissolution of gypsum.

$$AB_2 \Leftrightarrow A + 2B \qquad\qquad CaSO_4 \cdot 2H_2O \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$
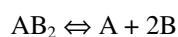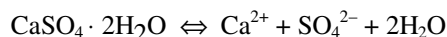
$$K_{AB_2} = \frac{a_A \cdot a_B^2}{a_{AB_2}} \qquad\qquad K = \frac{a_{Ca^{2+}} \cdot a_{SO_4^{2-}} \cdot a_{H_2O}^2}{a_{CaSO_4 \cdot 2H_2O}}$$

K is used for a variety of reactions with various designations in different textbooks. In all cases it remains as the thermodynamic constant K for any reaction under equilibrium conditions:

$K_{eq}$    The equilibrium thermodynamic reaction constant.
$K_T$    Equilibrium thermodynamic reaction constant. Subscript T is for thermodynamic constant.

$K_{10°}$    Reaction constant for a specified temperature.
$K_{sp}$    Solubility product, for mineral dissolution reactions.
$K_{diss}$    Dissociation reaction constant.
$K_{ex}$    Ion exchange reaction constant.

In qualitative terms, the value of $K_{sp}$ for mineral dissolution reactions provides an indication of solubility. Under equi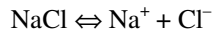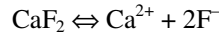librium conditions, high mineral solubility allows high concentrations of products in equilibrium with the solid phase. For example, the solubility products for halite and fluorite are:

$$NaCl \Leftrightarrow Na^+ + Cl^- \qquad\qquad CaF_2 \Leftrightarrow Ca^{2+} + 2F^-$$
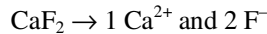
$$K = \frac{a_{Na^+} \cdot a_{Cl^-}}{a_{NaCl}} = 10^{1.58} \qquad\qquad K = \frac{a_{Ca^{2+}} \cdot a_{F^-}^2}{a_{CaF_2}} = 10^{-10.96}$$

For a first-order approximation, we can estimate the activity coefficients to be close to 1, which assumes that ion concentration is equal to ion activity ($a_i = m_i$). Substituting the stoichiometric relationship for these halides into the K-equation:

$$10^{1.58} = a_{Na} \cdot a_{Cl} \approx m_{Na} \cdot m_{Cl} \qquad\qquad 10^{-10.96} = a_F^2 \cdot a_{Ca} \approx m_F^2 \cdot m_{Ca}$$

$$NaCl \rightarrow 1\ Na^+ \text{ and } 1\ Cl^- \qquad\qquad CaF_2 \rightarrow 1\ Ca^{2+} \text{ and } 2\ F^-$$

$m_{Na} = m_{Cl}$ 
$10^{1.58} \approx m_{Cl} \cdot m_{Cl} \approx m_{Cl}^2$
$m_{Cl} \approx 10^{0.79}$ or 6.17 mol/kg

$m_{Ca} = \tfrac{1}{2} m_F$
$10^{-10.96} \approx m_F^2 \cdot m_{Ca} \approx m_F^2 \cdot \tfrac{1}{2} m_F$
$m_F \approx (2 \cdot 10^{-10.96})^{1/3} \approx 0.00028$ mol/kg

giving    $Cl^- \approx 219{,}000$ ppm        and        $F^- \approx 5.3$ ppm

Thus, a halite-saturated solution would be far more saline than water in equilibrium with fluorite. The precision of these calculations is improved by calculating the ionic strength, $I$, and then the activity coefficients, $\gamma$, as demonstrated below in Example 2-4. The actual aqueous concentrations of these ions are greater than their activities from $\gamma$ and $I$..

### *Gibb's free energy and determination of K*

Geochemical calculations are based on equilibrium thermodynamics – the interaction of molecules under the influence of heat. Geochemical reactions are governed by the changes of energy between reactants and products, expressed as *Gibbs free energy*. Reactions will tend to proceed towards a state of lower free energy, with a release of heat (heat content or enthalpy — H, in units of kJ/mol) or an increase in disorder (entropy — S, in units of kJ/mol·K), or some combination of both. :

$$\Delta G = \Delta H - T\Delta S$$

A geochemical system having a minimum of free energy, where $\Delta G = 0$ is considered to be in thermodynamic equilibrium.

All minerals, gases, geochemical species and the various phases of water itself have a measurable Gibbs free energy of formation $\Delta G°$, measured in kJ/mol. This is the change in free energy when forming one mole of the compound or ion from its component elements in their elemental states. By convention, all elements in their elemental state (e.g. $O_2$ or $Fe_{metal}$), as well as protons, $H^+$, and electrons, $e^-$, have $\Delta G° = 0$.

Compounds not in their elemental state will have positive or negative $\Delta G°$ values depending on whether they require or release energy in their formation from an elemental state. Sulfur species provide an example:

Sulfide, $S^{2-}$ $\qquad$ $\Delta G°_{S^{2-}} = 85.9$ kJ/mol

Elemental sulfur, S $\qquad$ $\Delta G°_{S} = 0$ kJ/mol

Sulfur dioxide, $SO_2$ $\quad$ $\Delta G°_{SO_2} = -300.1$ kJ/mol

Sulfate, $SO_4^{2-}$ $\qquad$ $\Delta G°_{SO_4^{2-}} = -744.0$ kJ/mol

Reduction of sulfur (valence 0) to sulfide (valence –II) requires energy and produces a combustible form of sulfur. By contrast, energy is released in converting native sulfur to $SO_2$ (valence +IV), as when a match is struck, or in oxidizing sulfide minerals like pyrite to $SO_4^{2-}$ (+VI), a reaction that provides energy for *Thiobacillus thiooxidans* bacteria.

From the standard Gibbs free energies of formation for reacting compounds, we can calculate the standard Gibbs free energy of any reaction $\Delta G°_r$, a value that allows determination of the equilibrium reaction constant K. The $\Delta G°_r$ (kJ/mol) is equal to the sum of $\Delta G°$ for all products minus the sum of all reactants:

$$\Delta G°_r = \sum \Delta G°_{products} - \sum \Delta G°_{reactants}$$

The standard Gibbs free energy of the reaction is related to the activities of the reacting components through the gas constant R (8.3143 J/mol·kelvin) and temperature (298 kelvin). Using the examples of reactions from above, the determination of K follows accordingly:

$$bB + cC \Leftrightarrow dD + eE \qquad\qquad CaSO_4 \cdot 2H_2O \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$
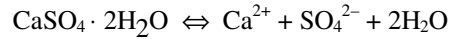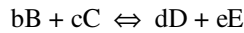
$$\Delta G°_r = -RT \ln \frac{a_D^d \cdot a_E^e}{a_B^b \cdot a_C^c} \qquad\qquad \Delta G°_r = -RT \ln \frac{a_{Ca^{2+}} \cdot a_{SO_4^{2-}} \cdot a_{H_2O}^2}{a_{CaSO_4 \cdot 2H_2O}}$$

$$K = \frac{a_D^d \cdot a_E^e}{a_B^b \cdot a_C^c} \qquad\qquad K_{gypsum} = \frac{a_{Ca^{2+}} \cdot a_{SO_4^{2-}} \cdot a_{H_2O}^2}{a_{CaSO_4 \cdot 2H_2O}}$$

$$\Delta G°_r = -RT \ln K \qquad\qquad \Delta G°_r = -RT \ln K_{gypsum}$$

Substitution of values for R and T, and converting from natural logarithm to $\log_{10}$ gives the simple relationship between the standard Gibbs free energy of reaction and the equilibrium reaction constant:

$$\log K = -\frac{\Delta G°_r}{5.708} \ (\Delta G \text{ in kJ/mol}) \qquad \text{or using calories,} \ \ \log K = -\frac{\Delta G°_r}{1.364} \ (\Delta G \text{ in kcal/mol})$$

The conversion for using free energy data in calories (1 Joule = 4.187 calories) is given as older textbooks use these units. Since $\Delta G°_r$ can be calculated from free energy data available for most geochemical species, the equilibrium constant, K, for any reaction can be determined. Gibbs free energy data for some common geochemical species and minerals are given in Table 2-4, below. These data have been compiled from various sources for the use of exercises in this chapter. In most applications, these data are included and used by geochemical computer programs for speciation and mineral solubility calculations.

Example 2-3   Determining equilibrium reaction constant K from $\Delta G°$ data

**Case 1:** *What is the solubility product $K_{sp}$ for gypsum?*

$$CaSO_4 \cdot 2H_2O \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$

$$K_{gypsum} = \frac{a_{Ca} \cdot a_{SO_4} \cdot a_{H_2O}^2}{a_{gypsum}} = a_{Ca^{2+}} \cdot a_{SO_4^{2-}}$$

$$\Delta G°_r = \Delta G°_{Ca^{2+}} + \Delta G°_{SO_4^{2-}} + 2\,\Delta G°_{H_2O} - \Delta G°_{gypsum}$$
$$= (-552.8) + (-744.0) + 2(-237.14) - (-1797.36)$$
$$= 26.28 \text{ kJ/mol}$$

$$\log K_{gypsum} = -\frac{\Delta G°_r}{5.708}$$

$$\log K_{gypsum} = -\frac{26.28}{5.708} = -4.60$$

Thus, $K_{gypsum} = 10^{-4.60}$

**Case 2:** What is the dissociation constant of water?

$$H_2O \Leftrightarrow H^+ + OH^-$$
$$\Delta G° = 0 + (-157.2) - (-237.14)$$
$$= 79.94 \text{ kJ/mol}$$

$$\log K_{H_2O} = -\frac{\Delta G°_r}{5.708}$$
$$= \frac{-79.94}{5.708}$$
$$= -14.00$$

$$K_{H_2O} = 10^{-14.00}$$

This result is no surprise, considering that the dissociation of pure water gives equal activities of $H^+$ and $OH^-$ :

$$10^{-14.00} \frac{a_{H^+} \cdot a_{OH^-}}{a_{H_2O}} = \frac{a_{H^+} \cdot a_{OH^-}}{1}$$

$$\therefore a_{H^+} = a_{OH^-} = 10^{-7.00}$$

With reaction constants, calculations can be made of mineral solubility, ion activities and concentrations at saturation, and geochemical speciation.

Example 2-4   Mineral dissolution and ion activity

How much gypsum can be dissolved in pure water (ignoring the effects of complex species such as $CaSO_4°$ or $HSO_4^-$)?

**Step 1**   Calculate the solubility product $K_{sp}$ for gypsum from Gibb's free energy data. From Example 2-3, this was determined to be $10^{-4.60}$ at 25°C.

**Step 2**   Calculate the activities of $Ca^{2+}$ and $SO_4^{2-}$ following the dissolution of gypsum to saturation at 25°C.

From the gypsum dissolution equation above, we have:

$$K_{gypsum} = \frac{a_{Ca^{2+}} \cdot a_{SO_4^{2-}} \cdot a_{H_2O}^2}{a_{gypsum}} = 10^{-4.60}$$

$A_{gypsum} = 1$ (activities of pure solids are 1 by convention)

$a_{H_2O} = 1$ (also by convention)

$\therefore a_{Ca^{2+}} \cdot a_{SO_4^{2-}} = 10^{-4.60}$

and so $a_{Ca^{2+}} = a_{SO_4^{2-}} = 10^{-2.30} = 0.005$

**Step 3** These calculated activities are less than the concentration of $Ca^{2+}$ and $SO_4^{2-}$ and so cannot be converted to mg/kg or mg/L until first corrected to $m$ with the activity coefficient $\gamma$. This is done by iteration, calculating $I$, then $\gamma$ values, and then $m$ for concentration. The solution is simplified considering both $Ca^{2+}$ and $SO_4^{2-}$ have $z = 2$, and for gypsum dissolution, $m_{Ca} = m_{SO_4}$. As a first approximation of $I$, assume that $a = m$.

$I \cong \tfrac{1}{2} (m_{Ca} \times 2^2 + m_{SO_4} \times 2^2)$

$\cong 0.5 (0.005 \times 4 + 0.005 \times 4)$

$\cong 0.02$

Using Davies equation to calculate activity coefficients:

$$\log \gamma_{Ca} = \log \gamma_{SO_4} \frac{-0.5 \cdot 2^2 \sqrt{0.02}}{1 + 0.33(5.0)\sqrt{0.02}} + 0.3 \cdot 0.02 = -0.2233$$

$\gamma_{Ca} = \gamma_{SO4} = 0.60$

Then calculating molality from $m = \dfrac{a}{\gamma}$:

$$m_{Ca} = m_{SO_4} = \frac{a_{Ca}}{\gamma_{Ca}} = \frac{0.005}{0.60} = 0.0083 \text{ mol/kg}$$

Recalculating $I$ using this new estimate of molality, then $\gamma$ and $m$ again gives:

$I \cong 0.5 (0.0083 \times 4 + 0.0083 \times 4) = 0.033$

$\gamma_{Ca} = \gamma_{SO4} = 0.53$

$$m_{Ca} = m_{SO_4} = \frac{a_{Ca}}{\gamma_{Ca}} = \frac{0.005}{0.53} \, 0.0094 \text{ mol/kg} \quad (2^{nd} \text{ iteration})$$

Repeating the calculations:

$I \cong 0.5 (0.0094 \times 4 + 0.0094 \times 4) = 0.038$

$\gamma_{Ca} = \gamma_{SO4} = 0.52$

$m_{Ca} = m_{SO_4} = 0.0097 \text{ mol/kg} \qquad (3^{rd} \text{ iteration})$

By the $4^{th}$ iteration, these calculations have converged on a solution of 0.0098 mol/kg. Thus, 0.0098 moles or $0.0098 \times 172.2 = 1.7$g of gypsum (gfw = 172.2) can be dissolved per liter of fresh water.

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### *Mineral saturation index*

While most solute – water reactions attain equilibrium in seconds to minutes (e.g. dissociation of carbonic acid – $H_2CO_3 \Leftrightarrow HCO_3^- + H^+$) reactions that involve different phases such as mineral dissolution/precipitation reactions are kinetically impeded and are seldom in equilibrium. Many may be slowly moving towards equilibrium conditions, although changing temperature or changes in solute concentration with water movement may alter the geochemical environment and with it the state of mineral saturation. A simple calculation allows geochemists to assess whether a given mineral is close to or far from equilibrium with its solubility products. This is the mineral saturation index, SI, defined as the ratio of the ion activity product (IAP) to the solubility product $K_{sp}$.

$$SI = \frac{IAP}{K_{sp}}$$

Using again the example of gypsum dissolution:

$$IAP_{gypsum} = a_{Ca^{2+}} \cdot a_{SO_4^{2-}}$$
$$K_{sp} = 10^{-4.60}$$

$$SI = \frac{a_{Ca^{2+}} \cdot a_{SO_4^{2-}}}{10^{-4.60}} \qquad \text{or} \ \log SI = \log a_{Ca^{2+}} + \log a_{SO_4^{2-}} - (-4.60)$$

The saturation index can then provide a qualitative assessment of the degree of saturation of any mineral for a given solution, where:

$SI > 1$  or  $\log SI > 0$     mineral is supersaturated and can precipitate
$SI = 1$  or  $\log SI = 0$     mineral is in equilibrium with the solution
$SI < 1$  or  $\log SI < 0$     mineral is undersaturated, and will dissolve if present

The greater the deviation from unity, the greater is the degree of disequilibrium. As mineral saturations can vary by a few orders of magnitude, the logarithmic form ($\log SI$) is generally used.

The saturation index is a simplistic measure of saturation and does not take into account the temperature effects of mineral stability. For example, a low salinity solution with elevated concentration of $H_4SiO_4$ will be supersaturated with respect to quartz at 25°C. However, quartz will never precipitate at this low temperature. A higher salinity polymorph of quartz, say amorphous silica, will form instead. Similarly, gypsum will not precipitate from a solution at geothermal temperatures although it may be supersaturated, as anhydrite is the stable sulfate.

The use of SI does also not take into account the slow kinetics and nucleation problems of many reactions. Dolomite is a mineral that is often supersaturated in carbonate waters, although it is observed only in certain high salinity environments. Clay minerals are also slow to form due to the slow kinetics of feldspar weathering.

For most fundamental geochemical applications, the saturation index is a useful measure of saturation for minerals that are not kinetically impeded. The major low-temperature minerals in this group include the carbonates (principally calcite), the evaporite minerals, iron sulfide (mackinawite) and the oxy-hydroxides.

---

*Example 2-5   Determining the state of saturation of low temperature minerals. For groundwater with the following geochemical analysis, determine the saturation indices for calcite and gypsum.*

| | | | |
|---|---|---|---|
| T = 25°C | $Na^+$ = 180 ppm | $HCO_3^-$ = 250 ppm | |
| pH = 7.65 | $K^+$ = 18 ppm | $CO_3^{2-}$ = 0.8 ppm | |
| | $Ca^{2+}$ = 60 ppm | $SO_4^{2-}$ = 85 ppm | |
| | $Mg^{2+}$ = 22 ppm | $Cl^-$ = 280 ppm | |

**Step 1**   Determine $K_{calcite}$ and $K_{gypsum}$

$$\log K_{calcite} = = -\frac{\Delta G^{\circ}_r}{5.708}$$

$$\Delta G^{\circ}_{r \, calcite} = \Delta G^{\circ}_{Ca^{2+}} + \Delta G^{\circ}_{CO_3^{2-}} - \Delta G^{\circ}_{CaCO_3}$$

$$= (-552.8) + (-527.9) - (-1129.07)$$
$$= 48.37 \text{ kJ/mol}$$

$$\log K_{calcite} = -\frac{48.37}{5.708} = -8.47$$

$$\log K_{gypsum} = -4.60 \text{ (from Example 2-3)}$$

**Step 2**    Calculate $m$, for input species and then calculate $I$

|       | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $HCO_3^-$ | $CO_3^{2-}$ | $SO_4^{2-}$ | $Cl^-$ |
|-------|--------|-------|-----------|-----------|-----------|-------------|-------------|--------|
| ppm   | 180    | 18    | 60        | 22        | 250       | 0.80        | 85          | 280    |
| gfw   | 23     | 39.1  | 40.1      | 24.3      | 61        | 60          | 96          | 35.5   |
| $m$   | 0.0078 | 0.00046 | 0.0015  | 0.00091   | 0.0041    | $1.3 \cdot 10^{-5}$ | 0.00089 | 0.0079 |

$$I = \tfrac{1}{2}(\Sigma \, m_i \, z_i^2) = 0.017$$

**Step 3**    Using $I$, calculate $\gamma$ for all ions using the simplified Debye Hückel equation, and $a$ for each

|         | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $HCO_3^-$ | $CO_3^{2-}$ | $SO_4^{2-}$ | $Cl^-$ |
|---------|--------|-------|-----------|-----------|-----------|-------------|-------------|--------|
| $\gamma$ | 0.87  | 0.87  | 0.56      | 0.56      | 0.87      | 0.56        | 0.56        | 0.87   |
| $a$     | 0.0068 | 0.00040 | 0.00084 | 0.00051   | 0.0036    | $7.5 \cdot 10^{-6}$ | 0.00050 | 0.0069 |
| $\log a$ | -2.17 | -3.40 | -3.08    | -3.29     | -2.45     | -5.13       | -3.30       | -2.16  |

**Step 4**    Determine $\log SI_{calcite}$ and $\log SI_{gypsum}$

$$\log IAP/K_{calcite} = \log a_{Ca} + \log a_{CO_3} - (-8.47)$$
$$= -3.08 - 5.13 + 8.47$$
$$= 0.26$$
$$\log IAP/K_{gyp} = -3.08 - 3.30 + 4.60$$
$$= -1.78$$

This groundwater is slightly oversaturated with respect to calcite, and almost two orders of magnitude undersaturated with respect to gypsum. A possible scenario is that this water is dissolving gypsum and precipitating calcite through the common ion effect ($Ca^{2+}$).

---

*Temperature effect on K*

As K is a function of Gibbs free energy of reaction, it will naturally vary with temperature. It will also vary with pressure, although most applications of low temperature aqueous geochemistry are restricted to near surface environments for which standard pressure (1 atmosphere) is assumed. Adjustments to K for temperatures different from 25°C are made using standard enthalpy measurements for the reaction $\Delta H°_r$ and the Van't Hoff equation. The approach is based on the standard enthalpy H and entropy S of reaction ($\Delta H°_r$ in J/mol and $\Delta S°_r$ in J/mol · kelvin) and temperature T (kelvin) which relate to the standard Gibbs free energy of reaction according to:

$$\Delta G°_r = \Delta H°_r - T \, \Delta S°_r$$

and so    $\Delta H°_r - T \, \Delta S°_r = -RT \ln K$

However, to avoid inconsistencies within the various entropy and enthalpy databases, this equation is differentiated with respect to T and integrated over the range from 298 kelvin to the temperature of interest:

$$\log K_{T_2} = \log K_{298} + \frac{\Delta H°_r}{2.303\,R}\left(\frac{1}{298} - \frac{1}{T_{kelvin}}\right) \qquad \text{Van't Hoff equation}$$

This integration is valid for only a limited temperature range of about ±25°C (i.e. from 0° to 50°). Beyond this range, the change in enthalpy and entropy from standard values at 25°C to the new temperature must also be taken into account. Standard enthalpy of reaction data, $\Delta H°_r$, are available from the references for Gibb's free energy in Table 2-4.

Example 2-6   Calculation of $K_{sp}$ at a new temperature

*What is the solubility of calcite at 50°C?*

From Example 2-5, the solubility constant for calcite was determined.
        $\log K_{calcite} = -8.47$

The standard enthalpy of reaction for calcite dissolution comes from references given in Table 2-4.
        $\Delta H°_{calcite\ diss.} = -10.82$

$$\log K_{T_2} = \log K_{298} + \frac{\Delta H°_r}{2.303\,R}\left(\frac{1}{298} - \frac{1}{T_{kelvin}}\right)$$

$$= -8.47 + \frac{-10.82}{2.303\,(8.3143\cdot 10^{-3})}\left(\frac{1}{298} - \frac{1}{323}\right)$$

$$= -8.62$$

This value for $K_{50}$ is lower than $K_{25}$ indicating that calcite is less soluble at the higher temperature.

The effect of temperature varies for different minerals. The carbonates, for example, are more soluble at lower temperature. This is partly due to the increase in $K_{sp}$ at lower temperatures. It is also due to the increased solubility of $CO_2$ at lower temperature. By contrast, silicate minerals (felspars, quartz etc) are more soluble at higher temperature.

### *Formation of ion pairs*

In aqueous solutions, ions can have electrostatic interactions, which don't necessarily lead to bonding on a mineral surface. Such interaction between ions of opposite charge forms ion pairs – cations joined with a ligand (the anion of an ion pair). The product is a distinct aqueous species with reduced or neutral charge. Take for example a concentrated solution of the salt epsomite [$MgSO_4 \cdot 7H_2O$]. The high concentration of $Mg^{2+}$ and $SO_4^{2-}$ ions is such that a percentage will exist as the neutrally charged species $MgSO_4°$. This is still a dissolved species and not a mineral. Its dissociation is defined by a reaction constant K:

$$Mg^{2+} + SO_4^{2-} \Leftrightarrow MgSO_4°$$

$$K_{MgSO_4°} = \frac{a_{Mg^{2+}} \cdot a_{SO_4^{2-}}}{a_{MgSO_4°}} = 10^{-2.25}$$
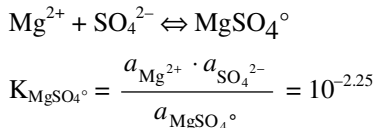
From this dissociation constant, it is apparent that when $a_{SO_4}$ is greater than $10^{-2.25}$ (or a concentration of some 900 mg/L) more Mg exists in the form of $MgSO_4°$ than as $Mg^{2+}$. The dissociation constants of the principal ion pairs that form in natural waters are given in Table 2-3. These values show that the doubly charged $Ca^{2+}$ and $Mg^{2+}$ cations form more stable ion pairs than does monovalent $Na^+$.

Table 2-3   Dissociation constants for common ion pairs

| Ion Pair | Log | Ion Pair | Log | Ion Pair | Log | Ion Pair | Log |
|----------|-----|----------|-----|----------|-----|----------|-----|

| | $K_{diss}$ | | $K_{diss}$ | | $K_{diss}$ | | $K_{diss}$ |
|---|---|---|---|---|---|---|---|
| $MgOH^+$ | −2.21 | $NaHCO_3^-$ | +0.25 | $NaCO_3^-$ | −1.27 | $NaSO_4^-$ | −0.70 |
| $CaOH^+$ | −1.40 | $MgHCO_3^+$ | −1.07 | $MgCO_3°$ | −2.02 | $MgSO_4°$ | −2.25 |
| | | $CaHCO_3^+$ | −1.11 | $CaCO_3°$ | −3.23 | $CaSO_4°$ | −2.31 |

In low salinity solutions, the degree of ion pairing is minimal, and has little effect on solute activities and the ionic strength of the solution. However, at higher ionic strength, the activities of individual ions diverge from their total (analytical) concentration due to the formation of ion pairs and ion complexes, which compete for the total amount of the ion in solution. For example, the total concentration of Ca in high salinity water is distributed among a number of complex ions:

$$m_{Ca\text{-total}} = m_{Ca^{2+}} + m_{CaSO_4°} + m_{CaOH^+} + m_{CaHCO_3^+} + m_{CaCO_3°} + m_{CaCl^+} + \dots$$

Determining the concentrations and activities of all relevant Ca species in a high salinity solution requires an iterative approach calculating $I$ and using a Ca mass balance equation together with the dissociation reaction equations, $\gamma$ and $a$ for all ion pairs. Only then can reasonable estimates of the activities of mineral precipitating compounds be made. The use of computer codes to solve these equations in multi-component solutions, discussed in a subsequent chapter, is of obvious benefit.

Table 2-4 Standard Gibbs free energy data for some common ions, compounds and minerals. Sources: Drever (1997), Langmuir (1997), Faure (1991). This table is not exhaustive and is for use in exercises in this book. 1 kcal = 4.18 4kJ.

| Species | $\Delta G°$ | Species | $\Delta G°$ | Species | $\Delta G°$ |
|---|---|---|---|---|---|
| $Ag^+$ | +77.1 | $Fe_2O_3$ hematite | −742.8 | $HS^-$ | 12.08 |
| | | | | $S^{2-}$ | 85.8 |
| $Al_2Si_2O_5(OH)_4$ kaolinite | −3799.7 | $FeCO_3$ siderite | −673.05 | $H_2S_{(aq)}$ | −27.83 |
| $Al(OH)_2$ gibbsite | −1157.9 | | | | |
| $Ba^{2+}$ | −555.36 | $FeS_2$ pyrite | −166.9 | $SO_{2(g)}$ | −300.1 |
| $BaCO_3$ witherite | −1132.21 | | | $SO_4^{2-}$ | −744.0 |
| $BaSO_4$ barite | −1362.2 | $H_2O$ liquid | −237.14 | $HSO_4^-$ | −755.3 |
| $HCO_3^-$ | −586.8 | $H_2O$ vapor | −228.58 | $SiO_2$ quartz | −856.3 |
| $CO_{2\,(gas)}$ | −394.4 | $OH^-$ | −157.2 | | |
| $CO_{2(aq)}$ | | | | | |
| $H_2CO_3$ | −623.14 | $K^+$ | −282.5 | | |
| $CO_3^{2-}$ | −527.9 | $KAlSi_3O_8$ K-feldspar | −3742.9 | $SiO_2$ amorphous | −849.1 |
| $CH_2O$ | −129.7 | | | | |
| $CH_4$ | −50.7 | | | | |
| $CH_3COOH$ | −392.52 | | | | |
| $Ca^{2+}$ | −552.8 | $KCl$ sylvite | −408.6 | $H_4SiO_4°$ | −1307.9 |
| $CaCO_3$ calcite | −1129.07 | | | $H_3SiO_4^-$ | −1251.8 |
| $CaF_2$ fluorite | −1176.3 | $Mg^{2+}$ | −455.4 | | |
| $CaMg(CO_3)_2$ dolomite | −2161.7 | $Mg(OH)_2$ brucite | −833.51 | $H_2SiO_4^{2-}$ | −1176.6 |
| $CaSO_4$ anhydrite | −1321.98 | $MgCO_3$ magnesite | −1012.1 | $Sr^{2+}$ | −563.83 |
| $CaSO_4 \cdot 2H_2O$ gypsum | −1797.36 | $Mn^{2+}$ | −228.1 | $SrCO_3$ strontianite | −1144.73 |
| $Ca_5(PO_4)_3OH$ apatite | −6338.3 | $Mn(OH)_2$ pyrochroite | −616.5 | | |
| $CaAl_2Si_2O_5$ anorthite | −1310.0 | $MnOOH$ manganite | −133.3 | $SrSO_4$ celestite | −1345.7 |
| $Ca(OH)_2$ portlandite | −897.5 | | | | |
| $Cl^-$ | −131.2 | | | | |
| $F^-$ | −281.5 | $NH_{3(g)}$ | −16.5 | | |
| $Fe^{3+}$ | −8.56 | $NH_{3\,(aq)}$ | −26.5 | | |
| $Fe^{2+}$ | −82.88 | $NH_4^+$ | −79.31 | | |
| $Fe(OH)^{2+}$ | −233.2 | $NO_3^-$ | −108.74 | | |
| $Fe(OH)_2^+$ | −450.5 | $NO_2^-$ | −32.2 | | |
| $Fe(OH)_3°$ | −648.3 | $Na^+$ | −262.0 | | |

| | | | | |
|---|---|---|---|---|
| $Fe(OH)_4^-$ | –833.83 | $NaAlSi_3O_8$ albite | –3711.5 | |
| $Fe(OH)_2$ amorphous | –486.5 | $NaCl$ halite | –384.14 | |
| $Fe(OH)_3$ ferrihydrite | –692.07 | | | |

## REDOX REACTIONS

The reactions studied so far involve the dissociation of minerals and compounds by acid – base reactions involving the exchange of protons and hydroxides. A second class of reactions involves the exchange of electrons — $e^-$. Unlike acid – base reactions, for which $H^+$ occurs in solution (usually as $H_3O^+$) with a measurable activity — pH, electrons do not occur freely in solution. They are exchanged through complementary reduction and oxidation (redox) reactions. Redox reactions have a tremendous impact on the aqueous form for a given element, which affects its solubility and participation in geochemical reactions.

Redox reactions also differ from acid – base reactions by their greater transfers of free energy. Take photosynthesis, which produces carbohydrate, the building block of sugars and cellulose:

$$CO_2 + H_2O \rightarrow O_2 + CH_2O$$
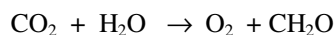
$$\Delta G°_r = (0 - 129.7) - (-394.4 - 237.14) = 501.84 \text{ kJ/mol}$$

This reaction is endothermic, requiring a considerable input of energy (photons) to proceed. The reverse of this reaction is respiration (or combustion) which releases this energy for animal life. The basis of the reaction is the change of redox state of carbon. As $CO_2$, carbon is in the +IV state, and is reduced to the O valence state when converted to $CH_2O$.

Redox reactions also differ from acid – base reactions by their kinetic nature. Redox reactions tend to be unidirectional rather than forward and backward as required for equilibrium. In fact, redox reactions most often require some sort of catalyst. Bacteria commonly derive energy from various redox reactions, thereby catalyzing a reaction that would otherwise be kinetically impeded. This occurs in both natural waters and in polluted settings such as landfill leachates, septic systems and agricultural settings.

Before looking too closely at the series of redox reactions that characterize natural systems, let's first see what is involved in a redox reaction from a thermodynamic perspective.

### Redox half-reactions

Reduction of an element involves the gain of electrons to fill the outer valence shell. When it is oxidized, electrons are removed. Free electrons in solution are not permitted, and so these reactions must occur in pairs. Paired reduction and oxidation reactions (redox pairs) allow the transfer electrons between the participating elements. The oxidant in a redox reaction is referred to as the electron acceptor and the species that is oxidized is the electron donor. The oxidation of organic matter by elemental oxygen ($O_2$), or respiration, is a good example. In respiration, elemental oxygen is the electron acceptor, and the organic carbon is the electron donor:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad \text{where O changes redox state from } O^0 \text{ to } O^{2-} (\Delta G°r = -474.3)$$

and the oxidation of organic matter (represented by simple carbohydrate):

$$CH_2O + H_2O \rightarrow CO_2 + 4e^- + 4H^+ \qquad \text{where C changes redox state from } C^0 \text{ to } C^{4+} (\Delta G°_r = -27.54)$$
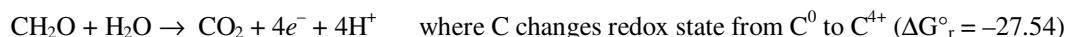
By combining these two reactions, the electrons and protons cancel, giving the overall redox reaction:

$$O_2 + CH_2O \rightarrow CO_2 + H_2O \qquad \text{with } \Delta G°_r = -501.84 \text{ kJ/mol}$$

$$\text{and } \log K = -\frac{-501.8}{5.708} = 87.9 \qquad\qquad K = \frac{P_{CO_2}}{P_{O_2} \cdot a_{CH_2O}} = 10^{87.9}$$

The negative free energy of the reaction indicates that the reaction is exothermic. Further, the very high reaction constant demonstrates that carbohydrate be thermodynamically stable only in the absence of $O_2$.

Other electron acceptors are found in natural waters, including nitrate $NO_3^-$, sulfate $SO_4^{2-}$, $Mn^{4+}$, $Fe^{3+}$ and even $CO_2$. In the absence of free $O_2$, these and other electron acceptors can oxidize organic matter. Table 2-5 gives the common species and their oxidation states for the principal redox-sensitive elements in natural waters.

Table 2-5   Common forms and oxidation states of the important redox elements in natural waters

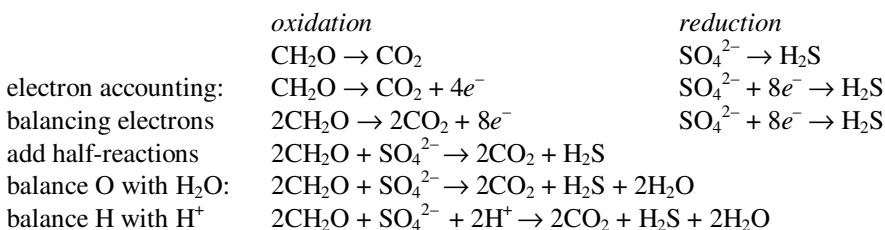| H | C | N | O | S | Mn | Fe |
|---|---|---|---|---|---|---|
| $H_2 - H^0$ | $CO_2 - C^{4+}$ | $NO_3^- - N^{5+}$ | $O_2 - O^0$ | $SO_4^{2-} - S^{6+}$ | $MnO_2 - Mn^{4+}$ | $Fe(OH)_2^+ - Fe^{3+}$ |
| $H^+$ | $HCO_3^- - C^{4+}$ | $NO_2^- - N^{3+}$ | $H_2O_2 - O^-$ | $S - S^0$ | $HMnO_2^- - Mn^{2+}$ | $Fe(OH)_3 - Fe^{3+}$ |
| $OH^- - H^+$ | $CH_2O - C^0$ | $N_2 - N^0$ | $H_2O - O^{2-}$ | $FeS_2 - S^{1-}$ | $Mn(OH)_2 - Mn^{2+}$ | $Fe_2O_3 - Fe^{3+}$ |
| $H_2O - H^+$ | $CH_3OH - C^{2-}$ | $NH_4^+ - N^{3-}$ | $OH^- - O^{2-}$ | $H_2S - S^{2-}$ | | $Fe(OH)^+ - Fe^{2+}$ |
| $CH_2O - H^+$ | $CH_4 - C^{4-}$ | | $CH_2O - O^{2-}$ | $FeS - S^{2-}$ | | $Fe(OH)_2 - Fe^{2+}$ |

Of these redox sensitive species, the most common redox pairs, with number of electrons transferred, include:

| | | | |
|---|---|---|---|
| $O_2/H_2O$ | $e^- = 2$ | $SO_4^{2-}/H_2S$ | $e^- = 8$ |
| $CO_2/CH_2O$ | $e^- = 4$ | $SO_4^{2-}/FeS$ | $e^- = 8$ |
| $CO_2/CH_4$ | $e^- = 8$ | $NO_3^-/N_2$ | $e^- = 5$ |
| $Fe(OH)_3/Fe^{2+}$ | $e^- = 1$ | $NO_3^-/NH_4^+$ | $e^- = 8$ |

In writing and balancing redox reactions, it is useful to write them as half reactions first, balance the electron transfer, then add them together to balance oxygen and hydrogen. Take, for example, the oxidation of organic carbon, $CH_2O$, using sulphate as an electron acceptor. In this case, methane is oxidized to $CO_2$ and sulphate is reduced to hydrogen sulphide:

|  | *oxidation* | *reduction* |
|---|---|---|
| | $CH_2O \rightarrow CO_2$ | $SO_4^{2-} \rightarrow H_2S$ |
| electron accounting: | $CH_2O \rightarrow CO_2 + 4e^-$ | $SO_4^{2-} + 8e^- \rightarrow H_2S$ |
| balancing electrons | $2CH_2O \rightarrow 2CO_2 + 8e^-$ | $SO_4^{2-} + 8e^- \rightarrow H_2S$ |
| add half-reactions | $2CH_2O + SO_4^{2-} \rightarrow 2CO_2 + H_2S$ | |
| balance O with $H_2O$: | $2CH_2O + SO_4^{2-} \rightarrow 2CO_2 + H_2S + 2H_2O$ | |
| balance H with $H^+$ | $2CH_2O + SO_4^{2-} + 2H^+ \rightarrow 2CO_2 + H_2S + 2H_2O$ | |

This reaction can be further resolved, considering that in the products, $CO_2$ will certainly hydrate and dissociate to produce bicarbonate, particularly considering that $H^+$ is being consumed on the left side:

$$2CH_2O + SO_4^{2-} + 2H^+ \rightarrow 2H_2CO_3 + H_2S$$
$$2CH_2O + SO_4^{2-} + 2H^+ \rightarrow 2HCO_3^- + H_2S + 2H^+$$
$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S$$
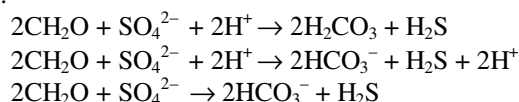
Example 2-7   Balancing redox reactions

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*Write a reaction for the oxidation of methane to bicarbonate with sulfate.*

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + H_2S$$

| | | |
|---|---|---|
| redox half reactions | $CH_4 \rightarrow HCO_3^-$ | $SO_4^{2-} \rightarrow H_2S$ |
| electron accounting: | $CH_4 \rightarrow HCO_3^- + 8e^-$ | $SO_4^{2-} + 8e^- \rightarrow H_2S$ |
| add the half-reactions | $CH_4 + SO_4^{2-} \rightarrow HCO_3^- + H_2S$ | |
| balance O with $H_2O$: | $CH_4 + SO_4^{2-} \rightarrow HCO_3^- + H_2S + H_2O$ | |
| balance H with $H^+$ | $CH_4 + SO_4^{2-} + H^+ \rightarrow HCO_3^- + H_2S + H_2O$ | |


*Write a reaction for the oxidation of pyrite with atmospheric (elemental) oxygen.*

$$FeS_2 + O_2 \rightarrow Fe^{2+} + SO_4^{2-}$$

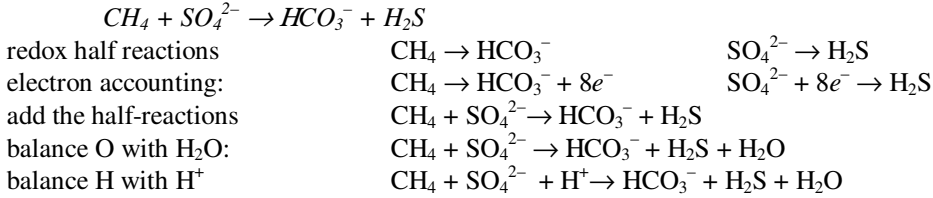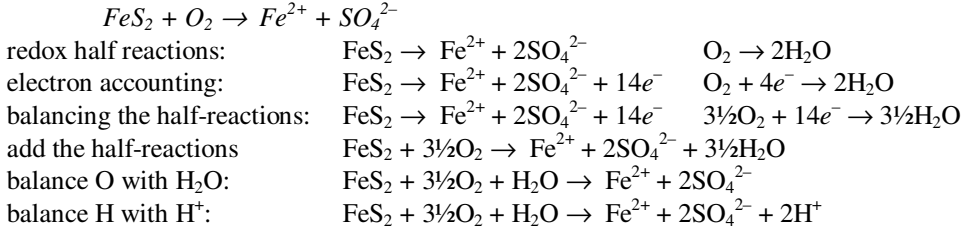| | | |
|---|---|---|
| redox half reactions: | $FeS_2 \rightarrow Fe^{2+} + 2SO_4^{2-}$ | $O_2 \rightarrow 2H_2O$ |
| electron accounting: | $FeS_2 \rightarrow Fe^{2+} + 2SO_4^{2-} + 14e^-$ | $O_2 + 4e^- \rightarrow 2H_2O$ |
| balancing the half-reactions: | $FeS_2 \rightarrow Fe^{2+} + 2SO_4^{2-} + 14e^-$ | $3\tfrac{1}{2}O_2 + 14e^- \rightarrow 3\tfrac{1}{2}H_2O$ |
| add the half-reactions | $FeS_2 + 3\tfrac{1}{2}O_2 \rightarrow Fe^{2+} + 2SO_4^{2-} + 3\tfrac{1}{2}H_2O$ | |
| balance O with $H_2O$: | $FeS_2 + 3\tfrac{1}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-}$ | |
| balance H with $H^+$: | $FeS_2 + 3\tfrac{1}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$ | |

---

### Electron activity – pe

Although aqueous redox reactions always take place in pairs, we can nonetheless write equilibrium half reactions. Doing so allows us to express redox equilibrium in terms of the activities of the reduced and oxidized species, and the electron activity, $a_{e^-}$. Although free electrons do not exist in solution, we can think of electron activity in terms of the demand for electrons, which would then be provided or consumed by the complementary redox half reaction. A high electron activity would characterize a solution with a high concentration of reduced species, such as $Fe^{2+}$ or $HS^-$. Using the pH convention, electron activity is expressed as the negative log of the electron activity, p$e$:

$$pe = -\log a_{e^-}$$

Using a generic reaction and the example of $O_2$:

$$Red \Leftrightarrow Ox + ne^- \qquad\qquad \tfrac{1}{2}O_2 + 2e^- + 2H^+ \Leftrightarrow H_2O$$
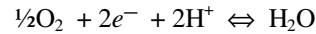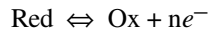
$$\log K = -\frac{\Delta G^\circ{}_r}{2.3RT} = \frac{\Delta G^\circ{}_{Ox} - \Delta G^\circ{}_{Red}}{2.3RT} \qquad \log K = -\frac{\Delta G^\circ{}_r}{5.708} = -\frac{-237.2}{5.708} = 41.55$$

$$K = \frac{a_{Ox} \cdot a_{e^-}^n}{a_{Red}} \qquad\qquad K = \frac{a_{H_2O}}{P_{O_2}^{1/2} \cdot a_{e^-}^2 \cdot a_{H^+}^2} = 10^{41.55}$$

$$a_{e^-} = \left(\frac{K \cdot a_{Red}}{a_{Ox}}\right)^{1/n} \qquad\qquad \log a_{e^-} = \left(\frac{a_{H_2O}}{P_{O_2}^{1/2} \cdot a_{H^+}^2 \cdot K}\right)^{1/2}$$

$$\log a_{e^-} \;=\; \frac{1}{n}\left(\log K + \log \frac{a_{Red}}{a_{Ox}}\right) \qquad\qquad \log a_{e^-} = \tfrac{1}{2}\log a_{H_2O} - \tfrac{1}{4}\log P_{O_2} - \log H^+ - 20.78$$

$$pe \;=\; \frac{1}{n}\left(\log \frac{a_{Ox}}{a_{Red}} - \log K\right) \qquad\qquad pe = 20.78 - pH + \tfrac{1}{4}\log \frac{P_{O_2}}{a_{H_2O}}$$

and for single electron transfers:    as $a_{H_2O} \approx 1$, this simplifies to:

$$pe = \log \frac{a_{Ox}}{a_{Red}} - \log K \qquad\qquad pe = 20.78 - pH + \tfrac{1}{4}\log P_{O_2}$$

This equation defines the $pe - pH$ conditions for the stability of water for a given $P_{O_2}$. Plotted on a $pe - pH$ diagram for a $P_{O_2}$ of 1 atmosphere, this line divides the lower $pe$ zone where water is stable from the high $pe$ zone where $H_2O$ is oxidized to $O_2$. For such conditions to exist, there would have to be a strong oxidant, such as fluorine gas, $F_2$, to react with water and produce $O_2$. More commonly, this reaction occurs by electrolysis where an electrical current passing through water produces $O_2$ at the positively charged anode by taking electrons from $O^{2-}$ in $H_2O$. This reaction, however, does not take place in natural waters.

The lower stability limit for water is defined by the reduction of water to hydrogen gas (elemental hydrogen) according to the reaction:

$$H_2O + e^- \Leftrightarrow \tfrac{1}{2}H_2 + OH^-$$

$$\log K = -\frac{-157.2 + 237.14}{5.708} = -14.0$$

$$10^{-14.0} = \frac{P_{H_2}^{\frac{1}{2}} \cdot a_{OH^-}}{a_{H_2O} \cdot a_{e^-}}$$

$$-14.0 = \tfrac{1}{2}\log P_{H_2} + \log a_{OH^-} - \log a_{e^-}$$

$$pe = -14.0 - \tfrac{1}{2}\log P_{H_2} - (-14 - \log a_{H^+})$$

$$= -\tfrac{1}{2}\log P_{H_2} - pH$$

Plotted for a $P_{H_2}$ of 1 atmosphere (Fig. 2-11) this defines the lower limit of $H_2O$ stability. At electron activities greater than those along this line (more negative $pe$) the $H^+$ in $H_2O$ is reduced to produce $H_2$ gas. This reaction is hydoxide-generating and can in fact take place in natural waters. The hyperalkaline springs in the Sultanate of Oman are an example (Fritz et al., 1992) where natural groundwaters with pH 11.6 are discharging $H_2$ gas produced by low-temperature serpentinization of ultramafic rocks.
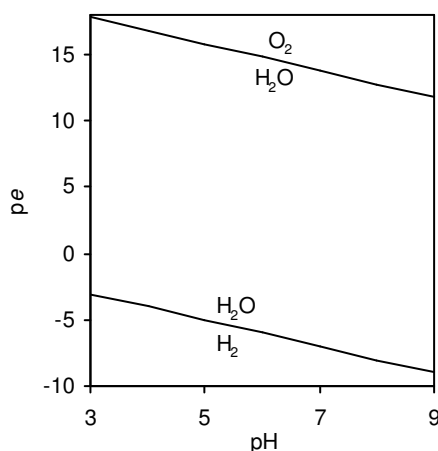
Fig. 2-11   p$e$ – pH diagram showing the stability field of water

Example 2-8   Calculating p$e$ from redox pair activity ratios

*What is the pe for a solution at neutral pH with a sulfate activity, $a_{SO_4^{2-}} = 10^{-2}$ (~960 ppm) and sulfide activity, $a_{H_2S_{(aq)}} = 10^{-3}$ (34 ppm)?*

writing the half-reaction:    $SO_4^{2-} + 8e^- \rightarrow H_2S_{(aq)}$
and balancing it:             $SO_4^{2-} + 8e^- + 10H^+ \rightarrow H_2S_{(aq)} + 4H_2O$

determining the reaction constant:    $\Delta G°_r = -27.83 + 4(-237.14) - (-744.0) = -232.39$ kJ/mol

$$\log K = -\frac{\Delta G°_r}{5.708} = -\frac{-232.39}{5.708} = 40.7$$

$$K_{SO_4^{2-}\text{-}H_2S} = \frac{a_{H_2S}}{a_{SO_4^{2-}} \cdot a_{e^-}^8 \cdot a_{H^+}^{10}} = 10^{40.7}$$

substituting redox species activities:    $8 \log a_e = \log a_{H_2S} - \log a_{SO_4^{2-}} - 10 \log a_{H^+} - 40.7$
$= \log (0.001) - \log (0.01) - 10 (-7) - 40.7$
$= 28.3$
$\log a_e = 3.54$
$pe = -3.54$

Note that by changing the activity of either $H_2S$ or $SO_4^{2-}$ has little effect on the p$e$, which is governed largely by the redox reaction constant, K. For example, increasing the activity of $H_2S_{(aq)}$ even by an order of magnitude (e.g. $a_{H_2S_{(aq)}} = 10^{-2}$) only shifts the p$e$ to $-3.67$.

### *Measuring the redox state of solutions – Electromotive potential (Eh)*

Measuring the redox state of a solution for redox reactions is similar to measuring pH for acid-base reactions. However, it is incorrect to assume that a single redox measurement characterizes the various redox reactions going on in solution. Nonetheless, measuring redox does provide an indication of the relative redox state of the water.

As we saw above, the oxidation of organic carbon drives redox evolution towards lower and lower p$e$ values where the reduced species of a redox pair is favored. This increase in electron activity cannot be directly measured, as there are no free electrons in solution. We can, however, measure the tendency of the solution to give or take electrons if another half-cell is connected. This is the electromotive potential E of the solution. Any redox half-reaction (or half-cell, e.g. $SO_4^{2-}/HS^-$ or $Fe^{3+}/Fe^{2+}$) has an electromotive potential (E) which is proportional to the activity ratio of the oxidized and reduced species in the half-cell reaction:

$$\text{Red} \Leftrightarrow \text{Ox} + \text{n}e^- \qquad\qquad\qquad Fe^{2+} \Leftrightarrow Fe^{3+} + e^-$$

$$E_{\text{half-cell}} \propto \frac{a_{\text{ox}}}{a_{\text{red}}} \qquad\qquad\qquad E_{Fe^{3+/2+}} \propto \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

The standard electromotive potential of a redox half-cell, E° is related to Gibb's free energy of reaction through Faraday's constant $\Im$ (96.485 kJ per volt-gram equivalent):

$$E°_{\text{half-cell}} = \frac{\Delta G°_{\text{half-cell}}}{\text{n}\Im} \qquad\qquad E°_{Fe^{3+/2+}} = \frac{-8.56 + 82.88}{96.485} = 0.77 \text{ volts}$$

Here, all components have activities of 1 mole/L and temperature of 25°C (standard conditions). Note that if the electron transfer reaction is written with the electrons on the right, this equation is positive (inverse). In real systems, we seldom observe activities of 1, and so the measured potential E is related to the standard potential through the reaction constant K (recalling that $\Delta G°_r = -RT \ln K$):

$$E_{\text{half-cell}} = E°_{\text{half-cell}} + \frac{RT \ln K_{\text{half-cell}}}{\text{n}\Im} \qquad\qquad E_{Fe^{3+/2+}} = 0.77 + \frac{RT \ln K_{Fe^{3+/2+}}}{\text{n}\Im}$$

$$= E°_{\text{half-cell}} + \frac{0.0083143 \cdot 298 \cdot \ln\left(\frac{a_{Ox} \cdot a_{e^-}^{\text{n}}}{a_{Red}}\right)}{\text{n} \cdot 96.49} \qquad\qquad = 0.77 + 0.059 \log \frac{a_{Fe^{3+}} \cdot a_{e^-}}{a_{Fe^{2+}}}$$

If we measure E against a half-cell of known potential, its value will be the measured potential less the potential of the reference half-cell. To simplify measurements, it is the standard hydrogen electrode (SHE) against which measured potentials are expressed. The standard hydrogen electrode is a platinum electrode connected to an acid solution with hydrogen gas bubbling through it ($P_{H_2}$ = 1 atm). Both $H^+$ and $e^-$ have unit activities in solution (pH = 0; p$e$ = 0). By convention the SHE has a potential of 0 volts. Measurements against the hydrogen electrode are then Eh measurements. The half-cell reaction in the hydrogen electrode is:

$$H^+ + e^- \rightarrow \tfrac{1}{2}H_2 \qquad\qquad E°_{SHE} = Eh = \frac{\Delta G°_r}{\text{n}\Im} = \frac{0 - (0 + 0)}{\text{n}\Im} = 0 \text{ volts}$$
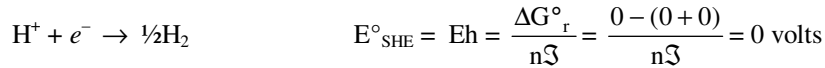
As the SHE has an electron activity of 1, when connected to the solution to measure its redox potential, the relation between measured potential and reaction constant K is simplified to:

$$Eh = E°_{\text{half-cell}} + \frac{0.059}{\text{n}} \cdot \log\left(\frac{a_{Ox}}{a_{Red}}\right) \qquad\qquad Eh = 0.77 - 0.059 \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

Using the SHE to measure the electromotive potential of a solution provides a measure of the activity ratio of the redox pair. The hydrogen electrode provides exactly what we are looking for – a way to measure in-situ redox conditions. With Eh measurements we can determine what redox pairs are active in solution. We can also determine the solubility of other redox sensitive species and minerals, and begin to predict the geochemical evolution of waters under different scenarios such as the addition of organic matter, or a sudden change in dissolved oxygen.

### *Measuring Eh*

Before heading off to the field to collect Eh data, some comments about the standard hydrogen electrode are needed. The SHE is a rather cumbersome piece of equipment, requiring an acid solution and supply of hydrogen gas. Field measurements are made using very compact electrodes that are based on metal-ion half-cell reactions. The most common is the silver-silver chloride electrode, which has a positive redox potential against the SHE:

$$Ag_{metal} + Cl^- \Leftrightarrow AgCl + e^- \qquad E°_{Ag/Ag^+} = 0.202 \text{ volts}$$

Measurements of E in waters are then converted to Eh using a temperature-corrected value for $E_{Ag/AgCl}$ (Table 2-6):

$$Eh = E_{measured} + E_{Ag/AgCl}$$

Table 2-6   Standard potentials for the Ag/AgCl redox electrode at different temperatures

| $T°C$ | $E_{Ag/AgCl}$ | $T°C$ | $E_{Ag/AgCl}$ | $T°C$ | $E_{Ag/AgCl}$ |
|---|---|---|---|---|---|
| 0 | 220 | 20 | 206 | 40 | 191 |
| 5 | 216 | 25 | 202 | 45 | 188 |
| 10 | 213 | 30 | 198 | 50 | 184 |
| 15 | 209 | 35 | 195 | 55 | 180 |

Unlike pH electrodes, which must be calibrated prior to use, a redox electrode responds directly to potential and so no calibration is possible. The electrode can, however, be tested in a standard solution to assure that it is reading correctly. Zobell's solution is commonly used. This is a mixture of 3.3 mM potassium ferrocyanide and 3.3 mM potassium ferricyanide in a 0.1 M KCl solution. At 25°C this solution has an Eh of 0.430 volts.  A Ag/AgCl electrode would measure 0.228 volts.

It must be remembered that an Eh measurement of a solution is a bulk measurement. The redox electrode will be responding to the dominant or most active redox pair. However, having measured Eh, it can be used in thermodynamic calculations of speciation and mineral solubility, which are based on p*e*. Using our generic case, we can relate the measured parameter Eh with the thermodynamic parameter p*e*.

$$Eh = E°_{half\text{-}cell} + \frac{2.3RT}{n\Im} \cdot log\left(\frac{a_{Ox}}{a_{Red}}\right) \qquad \text{and recalling: } E° = \frac{\Delta G°}{n\Im}$$

$$Eh = \frac{\Delta G°}{n\Im} + \frac{0.059}{n} \cdot log\left(\frac{a_{Ox}}{a_{Red}}\right)$$

Substitution with $\Delta G°_r = -0.059 \, logK$ gives:

$$Eh = -\frac{0.059 \, log \, K}{n} + \frac{0.059}{n} \cdot log\left(\frac{a_{Ox}}{a_{Red}}\right) = \frac{0.059}{n}\left(log\frac{a_{Ox}}{a_{Red}} - log \, K\right)$$

In this we recognize the pe relationship from above:

$$p e = \frac{1}{n}\left( \log \frac{a_{Ox}}{a_{Red}} - \log K \right)$$

Substitution then gives the fundamental relationship between pe and Eh :

$$Eh = 0.059 \, pe$$

### *Redox equilibria and measured Eh*

The concept of equilibrium in redox reactions requires some clarification. Unlike acid-base reactions, which are driven by $H^+$ activity — pH, redox reactions are driven by the activities of the redox species in solution. There is no general electron activity or pe of the solution as there are no free electrons. A redox measurement reflects the activity ratio — the ratio of the oxidized to reduced species for a given redox pair in the solution. So what is the Eh of a solution with more than one redox pair? The redox electrode will respond to the redox pairs with highest concentrations, and so is an approximation of the overall redox conditions. It can be used to calculate redox pairs (e.g. $SO_4^{2-}$ and $HS^-$ or $Fe^{3+}$ and $Fe^{2+}$) although it is more accurate to calculate pe from measured concentrations of these species. Take, for example, the water in Example 2-8. What would be its pe if there was also low but measurable dissolved oxygen – say 0.05 ppm? The pe for the oxygen redox reaction can be calculated from the equation derived above:

$$pe = 20.78 - pH + \frac{1}{4}\log P_{O_2}$$

the partial pressure, $P_{O_2}$, can be determined from the dissolved concentration using Henry's Law and $K_{O_2} = 10^{-2.89}$, from Table 2-8:

$$K_{O_2} = 10^{-2.89} = \frac{m_{O_2(aq)}}{P_{O_2}}$$

$$P_{O_2} = \frac{m_{O_2(aq)}}{10^{-2.89}} = \frac{0.05 / 32000}{0.00129} = 0.00121 = 10^{-2.92}$$

therefore:     $pe = 20.78 - (7) + \frac{1}{4}\log (-2.92)$
                          $= 13.05$

This pe, even for water that is very undersaturated with atmospheric oxygen (air satuated water has 8.71 ppm $O_2$ at 25°C; Table 2-8), is very much higher than the value of –3.67 calculated for $SO_4^{2-}/H_2S$ equilibrium in Example 2-8. The equilibrium $P_{O_2}$ for this water can be easily calculated:

$$pe = 20.78 - (7) + \frac{1}{4}\log (P_{O_2})$$
$$-3.67 = 20.78 - (7) + \frac{1}{4}\log (P_{O_2})$$
$$\log (P_{O_2}) = -69.8$$

Thus, the equilibrium concentration of $O_2$ in this water would be: $10^{-69.8} \cdot 10^{-2.89} = 6.53 \cdot 10^{-69}$ ppm — not much oxygen, and certainly less than measured. Such disequilibrium between redox pairs is typical of many waters, and can result from mixing of water from different strata in an open borehole or at a spring vent. It can also result from differences in the rates of bacterial activity which mediate most redox reactions in natural waters.

## SPECIATION AND MINERAL SOLUBILITY CODES

In the sections above, approaches were presented to determine ion activity and mineral solubility. The iterative calculation is to estimate ionic strength *I*, calculate the activity coefficients $\gamma$ and activities *a* for

dissolved species. When the solution has more than 2 or 3 components, this becomes a bookkeeping nightmare. Speciation codes simplify the calculation by keeping track of all the species present, apportioning the total concentration of the element in solution (say $Ca_{total}$) among all the aqueous species that contain it, and then determining the saturation index for all relevant minerals.

One of the earliest was WATEQ (Truesdell and Jones, 1974). This has been since upgraded to pc versions and to include trace elements and organic solutes (WATEQ4F; Ball and Nordstrom, 1991). This program is the basis of a variety of commercially available geochemical packages with user-friendly data input and output interfaces.

In the following, we will use the same water quality analysis as used in Example 2-5 to see the solution path followed by WATEQ4F and other programs, and to review the speciation and mineral solubility output.

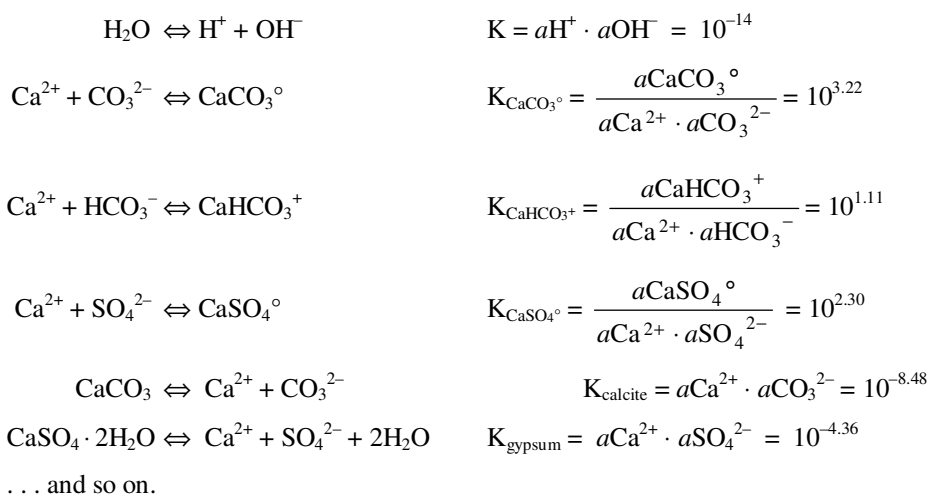Example 2-9   Input and output from WATEQ4F geochemical program

*Using the same water quality analysis used in Example 2-5, determine the speciation of the major elements and solubility of all relevant minerals.*

**Input** — Input of water quality data, including pH, temperature and element concentrations (total dissolved concentrations). Concentration units must be specified. Alkalinity can be entered as total alkalinity, alkalinity corrected for non-carbonate species (e.g. $HS^-$) or as bicarbonate and/or carbonate concentration.

| Species | pH | T°C | $Ca^{2+}$ | $Mg^{2+}$ | $Na^+$ | $K^+$ | $Cl^-$ | $SO_4^{2-}$ | $HCO_3^-$ | $CO_3^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Concentration (ppm) | 7.65 | 25 | 60 | 22 | 180 | 18 | 280 | 85 | 250 | 0.51 |

In this case, minor and trace element data are not included, and the program sets their concentration to 0. Other essential data include pH and water temperature. Optional data include the redox potential measurement as Eh or with a relevant redox pair (discussed in Chapter 5). Eh is not included in this example.

*Step 1* — establish all the relevant reactions and their related equilibrium constant equations for standard conditions, including reactions such as:

$$H_2O \Leftrightarrow H^+ + OH^- \qquad K = aH^+ \cdot aOH^- = 10^{-14}$$

$$Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3^{\circ} \qquad K_{CaCO_3^{\circ}} = \frac{aCaCO_3^{\circ}}{aCa^{2+} \cdot aCO_3^{2-}} = 10^{3.22}$$

$$Ca^{2+} + HCO_3^- \Leftrightarrow CaHCO_3^+ \qquad K_{CaHCO_3^+} = \frac{aCaHCO_3^+}{aCa^{2+} \cdot aHCO_3^-} = 10^{1.11}$$

$$Ca^{2+} + SO_4^{2-} \Leftrightarrow CaSO_4^{\circ} \qquad K_{CaSO_4^{\circ}} = \frac{aCaSO_4^{\circ}}{aCa^{2+} \cdot aSO_4^{2-}} = 10^{2.30}$$

$$CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-} \qquad K_{calcite} = aCa^{2+} \cdot aCO_3^{2-} = 10^{-8.48}$$

$$CaSO_4 \cdot 2H_2O \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \qquad K_{gypsum} = aCa^{2+} \cdot aSO_4^{2-} = 10^{-4.36}$$

. . . and so on.

*Step 2* — Set up mass balance equations for all input species, such as for $Ca_{total}$

$$mCa_{total} = mCa^{2+} + mCaSO_4^\circ + mCaCO_3^\circ + mCaOH^+ + \ldots = 0.0015 \text{ mol/L (or 60 ppm Ca)}$$

*Step 3* — Use Van't Hoff Equation to determine $K_{eq}$ for all equations for sample temperature.

*Step 4* — Calculation of I using input concentrations (first estimate of I)

*Step 5* — Calculation of activity coefficients $\gamma$ for all relevant species, i.e.,

$\gamma Ca^{2+}$, $\gamma SO_4^{2-}$, $\gamma CaOH^+$, $\gamma CaHCO_3^+$ . . .

*Step 6* — Calculate the distribution of species for all input elements using the mass balance equations in a matrix with an equal number of equations and unknown species activities. This distribution of species will lower the ionic strength *I* by the addition of neutral and singly charged species.

*Step 7* — Calculation of new *I*, which is used to calculate new activity coefficients. The code then iterates through steps 6 and 7 until the change in the calculated activities of all species is below a given threshold.

*Step 8* — Calculation of mineral saturation indices as a ratio of the ion activity product over the equilibrium solubility constant:

$$\log \frac{IAP}{K_{eq}}$$

***Output*** — The output includes a reiteration of the input data, followed by characteristics of the water quality analysis including:

*Iteration calculations, in this case showing the successive changes to activities of selected ions:*

| Iteration | S1-AnalCO$_3$ | S2-AnalSO$_4$ |
|---|---|---|
| 1 | 1.118803E–04 | 1.736878E–04 |
| 2 | 2.161136E–06 | 3.950909E–06 |
| 3 | –2.630459E–08 | –8.519385E–08 |

*Electrical conductivity calculated from speciation data:*
Calc Cond =   1439.5  µS

*Charge balance (epm) for analytical (input) concentrations and for calculated (after speciation), as a check on the geochemical analysis. In this case, the error (5.1%) is less than 10% and so is an acceptable analysis.*

Analytical – epmCations = 13.1055          Analytical epmAnions = 13.7945
Percent difference in input cation/anion balance =  –5.1227
 Calc EPMCAT =    12.7179   Calc EPMAN =      13.4070   Percent difference in calc cation/anion balance =   –5.2756
 Total Ionic Strength    (T.I.S.) from input data =   0.01675
 Effective Ionic Strength (E.I.S.) from speciation =   0.01600

*Calculated TDS, ionic strength and gas partial pressures*

| TDS ppm | Ionic Strength | log $P_{CO_2}$ | $CO_2$ total | $a_{H_2O}$ |
|---|---|---|---|---|
| 895.5 | 0.01600 | –2.283 | 4.27E-03 | 0.9996 |

*Aqueous speciation of the input species, including activities and activity coefficients*

| Species | Anal. ppm | Calc. ppm | Anal. Molality | Calc. Molality | % of Total | Activity a | Activity Coef. $\gamma$ | –log Activity |
|---|---|---|---|---|---|---|---|---|

| Species | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $Ca^{2+}$ | 60 | 54.838 | 1.50E-03 | 1.37E-03 | 91.4 | 8.43E-04 | 0.6155 | 3.074 |
| $CaCO_{3\,aq}°$ | | 1.04 | | 1.04E-05 | 0.69 | 1.04E-05 | 1.0037 | 4.981 |
| $CaHCO_3^+$ | | 4.347 | | 4.30E-05 | 2.87 | 3.79E-05 | 0.8816 | 4.421 |
| $CaHSO_4^+$ | | 0.000002 | | 1.13E-11 | 0 | 9.94E-12 | 0.8816 | 11.003 |
| $CaOH^+$ | | 0.000404 | | 7.09E-09 | 0 | 6.25E-09 | 0.8816 | 8.204 |
| $CaSO_{4\,aq}°$ | | 10.264 | | 7.55E-05 | 5.04 | 7.57E-05 | 1.0037 | 4.121 |
| $Cl^-$ | 280 | 279.997 | 7.91E-03 | 7.91E-03 | 100 | 6.95E-03 | 0.879 | 2.158 |
| $CO_3^{2-}$ | 0.51 | 0.72 | 8.51E-06 | 1.20E-05 | 0.28 | 7.39E-06 | 0.6159 | 5.131 |
| $HCO_3^-$ | 250 | 242.816 | 4.10E-03 | 3.98E-03 | 93.33 | 3.53E-03 | 0.8859 | 2.452 |
| $H_2CO_{3\,aq}°$ | | 10.962 | | 1.77E-04 | 4.14 | 1.78E-04 | 1.0039 | 3.751 |
| $H^+$ | | 0.000025 | | 2.49E-08 | 0 | 2.24E-08 | 0.8976 | 7.65 |
| $K^+$ | 18 | 17.943 | 4.61E-04 | 4.59E-04 | 99.69 | 4.04E-04 | 0.879 | 3.394 |
| $KSO_4^-$ | | 0.196 | | 1.45E-06 | 0.31 | 1.28E-06 | 0.8816 | 5.894 |
| $Mg^{2+}$ | 22 | 20.019 | 9.06E-04 | 8.24E-04 | 91 | 5.12E-04 | 0.6214 | 3.291 |
| $MgCO_{3\,aq}°$ | | 0.303 | | 3.60E-06 | 0.4 | 3.61E-06 | 1.0037 | 5.442 |
| $MgHCO_3^+$ | | 2.045 | | 2.40E-05 | 2.65 | 2.12E-05 | 0.8816 | 4.675 |
| $MgOH^+$ | | 0.003888 | | 9.42E-08 | 0.01 | 8.30E-08 | 0.8816 | 7.081 |
| $MgSO_{4\,aq}°$ | | 6.479 | | 5.39E-05 | 5.95 | 5.41E-05 | 1.0037 | 4.267 |
| $Na^+$ | 180 | 179.255 | 7.84E-03 | 7.80E-03 | 99.59 | 6.89E-03 | 0.883 | 2.162 |
| $NaCO_3^-$ | | 0.089 | | 1.08E-06 | 0.01 | 9.49E-07 | 0.8816 | 6.023 |
| $NaHCO_{3aq}°$ | | 1.143 | | 1.36E-05 | 0.17 | 1.37E-05 | 1.0037 | 4.864 |
| $NaSO_4^-$ | | 2.099 | | 1.76E-05 | 0.23 | 1.56E-05 | 0.8816 | 4.808 |
| $OH^-$ | | 0.008622 | | 5.07E-07 | 0 | 4.47E-07 | 0.8816 | 6.349 |
| $SO_4^{2-}$ | 85 | 70.754 | 8.86E-04 | 7.37E-04 | 83.24 | 4.50E-04 | 0.6109 | 3.346 |
| $HSO_4^-$ | | 0.000108 | | 1.11E-09 | 0 | 9.80E-10 | 0.8816 | 9.009 |

*The final calculation is the saturation index for each relevant mineral (minerals for which component species are present in input data) is calculated from species activities and solubility constants from step 3. In this case, only*

| Mineral | | log IAP/KT | log IAP | log KT |
|---|---|---|---|---|
| Anhydrite | $[CaSO_4]$ | −2.06 | −6.421 | −4.361 |
| Aragonite | $[CaCO_3]$ | 0.131 | −8.205 | −8.336 |
| Artinite | $[Mg_2(CO_3)(OH)_2·3(H_2O)]$ | −5.58 | 4.02 | 9.6 |
| Brucite | $[Mg(OH)_2]$ | −4.831 | 12.009 | 16.84 |
| Calcite | $[CaCO_3]$ | 0.274 | −8.205 | −8.48 |
| Dolomite (d) | $[CaMg(CO_3)_2]$ | −0.087 | −16.627 | −16.54 |
| Dolomite (c) | $[CaMg(CO_3)_2]$ | 0.463 | −16.627 | −17.09 |
| Epsomite | $[MgSO_4]$ | −4.498 | −6.638 | −2.14 |
| Gypsum | $[CaSO_4 · 2H_2O]$ | −1.84 | −6.421 | −4.581 |
| Halite | $[NaCl]$ | −5.902 | −4.32 | 1.582 |
| Huntite | $[CaMg_3(CO_3)_4$ | −3.503 | −33.471 | −29.968 |
| Hydromagnesite | $[Mg_5(CO_3)_4(OH)_2·4(H_2O)]$ | −12.917 | −21.679 | −8.762 |
| Magnesite | $[MgCO_3]$ | −0.393 | −8.422 | −8.029 |
| Mirabilite | $[Na_2SO_4 ·10(H_2O)]$ | −6.558 | −7.672 | −1.114 |
| Nahcolite | $[NaHCO_3]$ | −4.066 | −4.614 | −0.548 |
| Natron | $[Na_2CO_3 ·10(H_2O)]$ | −8.145 | −9.456 | −1.311 |
| Nesquehonite | $[Mg(HCO_3)(OH)·2(H_2O)]$ | −2.801 | −8.422 | −5.621 |
| Thenardite | $[Na_2SO_4]$ | −7.491 | −7.67 | −0.179 |
| Thermonatrite | $[Na_2CO_3 ·(H_2O)]$ | −9.58 | −9.455 | 0.125 |
| Trona | $[Na_3(CO_3)(HCO_3)·2(H_2O)]$ | −13.274 | −14.069 | −0.795 |

Comparing the results of the WATEQ4F calculations with those from the simplified hand calculations in Example 2-5 shows that for low salinity waters, the differences are minor, and due mainly to the inclusion of ion pairs (see speciation data, above) which reduce ionic strength and the activities of individual species. Given the ease with which the simplified calculations can be carried out using a spreadsheet program and tabulated input data, it is reasonable to use this approach for low salinity waters where ion pairs are not significant. Note that the simplified Debye-Hückel equation to determine activity coefficients, and the equations for calculating $K_{eq}$ at non-standard temperature can be embedded in the spreadsheet to simplify the calculations.

| *Parameter* | *Hand Calculations* | *WATEQ4F* |
|---|---|---|
| Ionic strength *I* | 0.017 | 0.016 |
| $a\text{Ca}^{2+}$ | 0.00084 | 0.000843 |
| log $SI_{calcite}$ | 0.26 | 0.274 |
| log $SI_{gypsum}$ | −1.78 | −1.84 |

Other comments on this example include:

- Most minerals are highly undersaturated in this low salinity water.

- The absence of silica from the input species has precluded all the silicate minerals including quartz and its polymorphs (e.g. chalcedony and amorphous silica), feldspars and clay minerals.

- No redox conditions or species were included with the input data, and so no redox sensitive minerals (sulfides, iron hydroxides) are reported in the output.


## ISOTOPE FRACTIONATION AND DISTILLATION

The distribution of the environmental isotopes throughout their different cycles in nature is controlled by the interplay of two processes. These are the *fractionation* of isotopes during any physical or chemical reaction, and the *distillation* of isotopes from reactant reservoir as the reaction consumes a significant fraction of this reservoir. These two processes are intermeshed, working together to partition isotopes into different reservoirs. This is always a difficult concept to grasp at the outset, but it is no more complicated than making moonshine. Take corn mash – that fermented liquid from the bottom of a silo. The concoction has too much water and not enough ethyl alcohol to satisfy most back-woods connoisseurs. But heating it up and condensing the vapors produces a high octane elixir that'll keep the fiddling and dancing going until dawn. Consider the alcohol to be the isotopes in the larger water reservoir of corn mash. As it is heated, the alcohol vaporizes faster than the water, and so the vapor is enriched in alcohol compared with the water and can be condensed to produce the moonshine with higher alcohol content than the mash. The enhanced vaporization of the alcohol over water is *fractionation*. At the outset of heating, with the production of the first few drops of moonshine, the alcohol content of the corn mash probably hasn't changed much. But as the work progresses, more and more alcohol is vaporized from the mash and the mash becomes measurably depleted in alcohol. This is *distillation*.

Another popular analogy for isotope fractionation is of the fellow clearing his rocky field to build a stone fence. The big stones (like $^{18}$O) make a stronger fence, and so it is these that he likes to use, leaving the small stones (i.e. $^{16}$O) behind in the field, and thus *fractionating* the stones between the field and his fence. As time goes on, his field (the reactant reservoir) is becoming noticeably depleted in big stones, due to *distillation* by his work. As he is now obliged to use the smaller remaining stones in his growing fence (the product reservoir) the newest end of the fence has a smaller average stone size, although still *enriched* in bigger stones compared to those in the greatly reduced reservoir of stones remaining the field.

The concentrations of environmental isotopes, like solutes, are controlled by thermodynamics. However, rather than using their concentrations in discrete phases and compounds, we use the isotopic ratio that changes during reaction. The result is an accumulation of isotopes on one side of a reaction, and a decrease on the other.

As observed in Chapter 1, the concentration or "abundance" of most naturally-occurring isotopes is very low. The variations in the abundance ratios are also very small, but measurable. For example, the $^{18}O/^{16}O$ abundance ratio is 0.002, and varies globally between about 0.0021 and 0.0019. These small variations in isotopic ratio are due to the slightly different rates of reaction for different isotopes of an element during physical and chemical processes. In 1947, Harold Urey published the theoretical basis for isotope fractionation as an exchange of isotopes between molecules that are participating in a reaction. Fractionation often takes place under equilibrium conditions. In this case we can define a fractionation factor, $\alpha$, for isotope reactions, which is no different than the equilibrium constant, K, presented in Chapter 2 for geochemical reactions.

As K defines mineral solubilities and solute concentrations in geochemical reactions, the fractionation factor, $\alpha$, establishes the isotope ratios in components of isotope exchange reactions. Unlike K, which can vary enormously (e.g. $10^{1.58}$ for dissociation of halite to $10^{-14}$ for the dissociation of water), isotope fractionation factors are for the most part very close to 1, as the partitioning of isotopes between compounds is very subtle.

### *Fractionation factor, $\alpha$*

Consider a simple change of state reactions for a generic compound, X to *X*, and for evaporation and condensation of water:

$$X \rightarrow X \qquad\qquad\qquad H_2O_{water} \rightarrow H_2O_{vapor}$$
$$\text{and}\quad X \rightarrow X \qquad\qquad\qquad H_2O_{vapor} \rightarrow H_2O_{water}$$

As the reaction comes to equilibrium conditions, the flux of reactant to product is matched by the flux of product converting to reactant in the reverse reaction such that some water is evaporating to vapor and some vapor is condensing to water.

$$X + X \leftrightarrow X + X \qquad\qquad H_2O_{water} + H_2O_{vapor} \leftrightarrow H_2O_{vapor} + H_2O_{water}$$
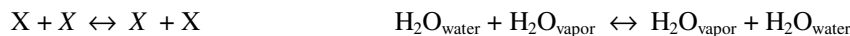
If we consider the reactants and products as only geochemical entities, then the thermodynamic reaction constant will be 1 (using square brackets to denote thermodynamic activity):

$$K_{X-X} = \frac{[X][X]}{[X][X]} = 1 \qquad\qquad K_{v-w} = \frac{[H_2O]_{vapor} \cdot [H_2O]_{water}}{[H_2O]_{water} \cdot [H_2O]_{vapor}} = 1$$

If we add isotopes to the reaction, there will be forward and backward exchange of isotopes until there is an equilibrium distribution with either the reactant or the product having more of the heavy isotope. In an equilibrium isotope exchange reaction, there is no change in the geochemistry of the solution, only an exchange of isotopes. Let's add isotopes to the above change of state reactions X and Y (using * for the heavy isotope), and the exchange of $^{18}O$ between water and water vapor:

$$X + {}^{a}X \leftrightarrow X + {}^{a}X \qquad\qquad H_2{}^{16}O_w + H_2{}^{18}O_v \leftrightarrow H_2{}^{18}O_w + H_2{}^{16}O_v$$

However, considering single-atom isotope exchange reactions, the thermodynamic reaction constant becomes:

$$K_{X-X} = \frac{[X][^aX]}{[X][^aX]}$$

$$= \frac{[^aX]}{[X]} \cdot \frac{[X]}{[^aX]} = \frac{\left(\dfrac{[^aX]}{[X]}\right)}{\left(\dfrac{[^aX]}{[X]}\right)}$$

$$= \frac{\left(\dfrac{[^aX]}{[X]}\right)}{\left(\dfrac{[^aX]}{[X]}\right)} = \frac{R_X}{R_X} = \alpha_{X-X}$$

$$K_{w-v} = \frac{[H_2{}^{18}O]_w [H_2{}^{16}O]_v}{[H_2{}^{16}O]_w [H_2{}^{18}O]_v}$$

$$= \frac{[^{18}O]_w}{[^{16}O]_w} \cdot \frac{[^{16}O]_v}{[^{18}O]_v}$$

$$= \frac{\left(\dfrac{^{18}O}{^{16}O}\right)_w}{\left(\dfrac{^{18}O}{^{16}O}\right)_v} = \frac{R_w}{R_v} = \alpha^{18}O_{w-v}$$

The equilibrium fractionation factor, $\alpha$, is simply the ratio of the isotopic ratio in two reacting phases or species. Like equilibrium constants, it is usually expressed as the isotope abundance ratio in the *product* (or right side of equation) over the isotope abundance ratio in the *reactant* (left side of equation).

$$\alpha_{product\text{-}reactant} = \frac{R_{product}}{R_{reactant}} \qquad\qquad \alpha^{18}O_{w-v} = \frac{R_w}{R_v}$$

If the reaction is written in reverse, the fractionation factor is simply the inverse value:

$$X + {}^aX \leftrightarrow X + {}^aX \qquad\qquad X + {}^aX \leftrightarrow X + {}^aX$$

$$\alpha_{X-X} = \frac{R_X}{R_X} \qquad\qquad \alpha_{X-X} = \frac{R_X}{R_X}$$

$$\alpha_{X-Y} = \frac{1}{\alpha_{X-X}}$$

The behavior of an isotope during physicochemical reaction is affected by its mass, because atoms with greater mass form slightly stronger bonds. Consequently, the heavier isotope is generally enriched in the more condensed phase (i.e. liquid over gaseous, or solid over liquid) or larger molecule. Take for example the evaporation and condensation of water molecules that (naturally) include both $^{18}O$ and $^{16}O$. Molecules of water are held together by weak hydrogen bonds whereas water vapor molecules diffuse through air. As there is slightly greater hydrogen bond strength for $H_2{}^{18}O–H_2O$ vs. $H_2{}^{16}O–H_2O$ bonds, it is the latter that will be more easily broken. The result is a greater concentration of $H_2{}^{16}O$ in the water vapor and more $H_2{}^{18}O$ in the water.

Example 2-10   Expressing the fractionation factor in terms of $\delta$–‰ values

*Using the example of $^{18}O$ fractionation between water and vapor, express the fractionation factor, $\alpha$, in terms of the $\delta^{18}O$ values of the water and vapor.*

$$\delta^{18}O_{water} = \left(\frac{\left(\dfrac{^{18}O}{^{16}O}\right)_{water}}{\left(\dfrac{^{18}O}{^{16}O}\right)_{VSMOW}} - 1\right) \cdot 1000$$

$$\left(\frac{^{18}O}{^{16}O}\right)_{water} = \left(\frac{^{18}O}{^{16}O}\right)_{VSMOW} \cdot \left(\frac{\delta^{18}O_{water}}{1000} + 1\right)$$

$$\left(\frac{^{18}O}{^{16}O}\right)_{vapor} = \left(\frac{^{18}O}{^{16}O}\right)_{VSMOW} \cdot \left(\frac{\delta^{18}O_{vapor}}{1000} + 1\right)$$

$$\alpha^{18}O_{water-vapor} = \frac{\left(\dfrac{^{18}O}{^{16}O}\right)_{water}}{\left(\dfrac{^{18}O}{^{16}O}\right)_{vapor}}$$

$$= \frac{\left(\dfrac{^{18}O}{^{16}O}\right)_{VSMOW} \cdot \left(\dfrac{\delta^{18}O_{water}}{1000} + 1\right)}{\left(\dfrac{^{18}O}{^{16}O}\right)_{VSMOW} \cdot \left(\dfrac{\delta^{18}O_{water}}{1000} + 1\right)}$$

$$= \frac{\left(\delta^{18}O_{water} + 1000\right)}{\left(\delta^{18}O_{vapour} + 1000\right)}$$

From Chapter 1, the isotope abundance ratio (e.g. $^{18}O/^{16}O$) does not vary enormously between different samples, and so the fractionation factor, $\alpha$, generally has a value close to 1. However, this value can be precisely measured or calculated, and so is expressed with a precision of 4 decimal places. However, isotope geochemistry is based on the variations of isotope concentrations, expressed as $\delta$–‰ values. To compare isotope fractionation with $\delta$–‰ values, we can express the fractionation factor, $\alpha$, in ‰ units, using the *enrichment factor*, $\varepsilon$:

$$\varepsilon = 1000\,(\alpha - 1)$$

With the enrichment factor, we can now do calculations involving fractionation and $\delta$–‰ values:

reactant $\leftrightarrow$ product

$$\varepsilon_{reactant\text{-}product} = \delta_{reactant} - \delta_{product}$$

and:    $$\varepsilon_{product\text{-}reactant} = -\varepsilon_{reactant\text{-}product}$$
$$= \delta_{product} - \delta_{reactant}$$

Example 2-11    Calculating $\delta^{18}O$ of water vapor in equilibrium with water

*A water sample has a $\delta^{18}O$ value of –4.5. It is in equilibrium with water vapor at 25°C. The fractionation factor at 25°C is 1.0093. What is the $\delta^{18}O$ value of the water vapor?*

$$\delta^{18}O_{water} = -4.5$$
$$\alpha^{18}O_{water\text{-}vapor} = 1.0093$$
$$\varepsilon^{18}O_{water\text{-}vapor} = (\alpha - 1) \cdot 1000$$

$$= (1.0093 - 1) \cdot 1000$$
$$= 9.3‰$$
$$\varepsilon^{18}O_{\text{water-vapor}} = \delta^{18}O_{\text{water}} - \delta^{18}O_{\text{vapor}}$$
$$\delta^{18}O_{\text{vapor}} = \delta^{18}O_{\text{water}} - \varepsilon^{18}O_{\text{water-vapor}}$$
$$= -4.5 - 9.3$$
$$= -13.8‰$$

∴ The $\delta^{18}O$ value for the water vapor is $-13.8‰$. The vapor is depleted in $^{18}O$ by 9.3‰, which is consistent with the pattern of isotope enrichment in the more condensed phase.

---

### *Fractionation and temperature*

Isotope fractionation is a thermodynamic process, and so is a function of temperature. Following from Urey's work, considerable effort has been made to establish the temperature relationship for isotope fractionation in various reactions such as water evaporation, condensation and freezing, aqueous geochemical reactions, mineral crystallization and others. These relationships are important in calculations of isotope fractionation in natural systems, which seldom takes place at constant temperature.

At high temperature, $\alpha$ is very close to 1, and departs from unity as the temperature of reaction decreases. For low temperature (<25°C) geochemical reactions, fractionation factors are greatest. This serves us well, as increased fractionation provides greater ranges in isotope values, which in turn improves the quality of our calculations and interpretation.

The temperature dependence of $\alpha$ is usually expressed by an exponential equation that produces a linear relationship when plotted as $\ln \alpha$ against the inverse of absolute temperature. As $\alpha$ is generally close to 1 for most isotope reactions, $\ln \alpha$ is then very close to 0. By multiplying $\ln\alpha$ by 1000, we then produce a fractionation factor in permil (‰) units that can be used directly with measured $\delta$–‰ data. This allows that the enrichment factor, $\varepsilon$, is essentially equal to $1000 \ln \alpha$:

$$\varepsilon = 1000 (\alpha - 1) \cong 1000 \ln \alpha$$

Thus, these two expressions of isotope fractionation are used interchangeably in most calculations. Only in a few isotope exchange reactions where the fractionation factor, $\alpha$, is very much different from 1, does this short-cut break down. For all practical work in isotope hydrology, and in this book, a simplification is used:

$$\varepsilon = 1000 \ln \alpha$$

As $\varepsilon$ is expressed in permil (‰) units, it can be used directly with $\delta$–‰ isotope data. Note that for equilibrium reactions in reverse (i.e. right to left), the fractionation factor, $\alpha$, and the enrichment factor are simply their inverse, therefore:

$$\alpha_{\text{product-reactant}} = 1/\alpha_{\text{reactant-product}} \qquad \varepsilon_{\text{product-reactant}} = -\varepsilon_{\text{reactant-product}}$$

A range of enrichment values, $\varepsilon^{18}O$ and $\varepsilon D$, for water-vapor fractionation calculated for different temperatures are given in Table 2-7 and are shown graphically in Fig. 2-12. Also given are the fractionation factors for $^{18}O$ and D exchange between water and ice and between ice and water vapor.

From these data, the trend towards increasing fractionation at lower temperatures is clear. Note the much greater degree of fractionation for D than for $^{18}O$ between water and vapor. This is a consequence of the mass difference of D over $^{1}H$, which is 100%. As $^{18}O$ is only 12.5% heavier than $^{16}O$, it will not be as strongly fractionated as D.

Table 2-7   Values for fractionation factors for $^{18}O$ and $^2H$ in water-vapor-ice reactions, based on equations given below.

| | Water-vapor | | Ice-water | |
|---|---|---|---|---|
| *T°C* | $\varepsilon^{18}O_{w\text{-}v}$ | $\varepsilon D_{w\text{-}v}$ | $\varepsilon^{18}O_{i\text{-}w}$ | $\varepsilon D_{i\text{-}w}$ |
| 0 | 11.6 ‰ | 106 ‰ | 2.8 ‰ | 20.6 ‰ |
| 25 | 9.3 ‰ | 76 ‰ | | |
| 50 | 7.5 ‰ | 55 ‰ | | |
| 75 | 6.1 ‰ | 39 ‰ | | |
| 100 | 5.0 ‰ | 27 ‰ | | |

Water-vapor: from Majoube (1971): (with T in kelvin)

$$\varepsilon^{18}O_{w\text{-}v} = 1.137(10^6/T^2) - 0.4156(10^3/T) - 2.0667$$
$$\varepsilon D_{w\text{-}v} = 24.844 (10^6/T^2) - 76.248 (10^3/T) + 52.612$$

Ice-water: O'Neil (1968)

Ice-vapor: $\varepsilon^{18}O_{ice\text{-}vapor} = \varepsilon^{18}O_{water\text{-}vapor} + \varepsilon^{18}O_{ice\text{-}water}$  and  $\varepsilon D_{ice\text{-}vapor} = \varepsilon D_{water\text{-}vapor} + \varepsilon D_{ice\text{-}water}$
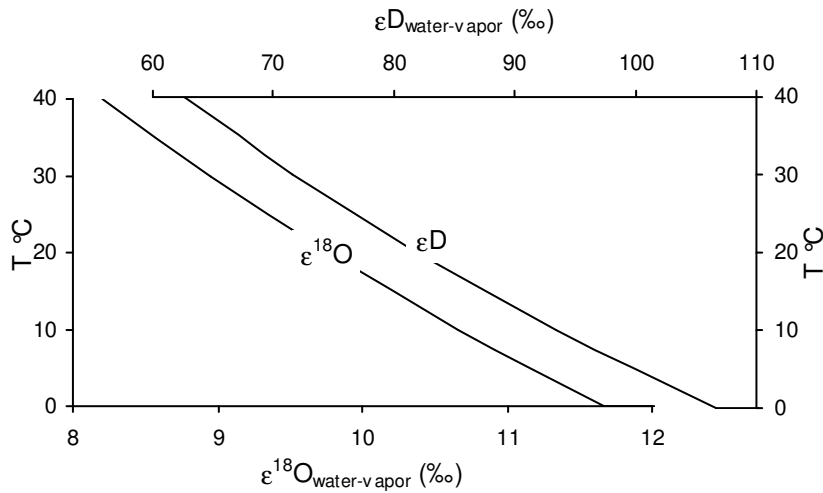


Fig. 2-12   Fractionation of $^{18}O$ and $^2H$ between water and water vapor.

Example 2-12   Temperature effect on fractionation

---

*What is the $\delta^{18}O$ for rain condensing at 20°C from a vapor mass that was formed by evaporation of seawater ($\delta^{18}O = 0‰$) at 25°C?*

$$H_2O_{seawater} \leftrightarrow H_2O_{vapor}$$
$$\delta^{18}O_{seawater} = 0‰ \text{ VSMOW}$$
$$\delta^{18}O_{seawater} = \delta^{18}O_{vapor} + \varepsilon^{18}O_{water\text{-}vapor @ 25}$$
$$\delta^{18}O_{vapor} = 0 - 9.3$$
$$= -9.3‰$$

The enrichment factor $\varepsilon^{18}O_{water\text{-}vapor}$ is taken to be equal to $10^3\ln \alpha$ (Table 2-7)

$$H_2O_{vapor} \leftrightarrow H_2O_{rain}$$
$$\delta^{18}O_{rain} = \delta^{18}O_{vapor} + \varepsilon^{18}O_{water\text{-}vapor}$$
$$= -9.3 + 9.7$$
$$= 0.4‰$$

For this example, evaporation and condensation were presumed to be under equilibrium conditions. While this is often the case for condensation, the formation of a vapor mass is generally more complicated, involving mixing of different vapor sources and partial rainout.

---

In this introduction, the fractionation of $^{18}O$ and $^{2}H$ in water and water vapor has been highlighted. The same principles of fractionation apply to other environmental isotopes in other geochemical systems. These will be introduced as we move from tracing the hydrological cycle to tracing geochemical evolution in natural waters.

### *Reservoir effects and Rayleigh distillation of isotopes*

Isotope fractionation during a geochemical reaction acts to partition isotopes between reservoirs. Recall our worker building his stone fence. Because he was selecting the light stones, his field gradually became enriched in the heavy stones. Subsequent fences build from this field would be built with more of the heavy stones, until there were no stones left in the field (the reaction is complete), and the final fence was built mainly with heavy stones. Isotopes behave in the same way with finite reservoirs.

Take, for example, a pond of water that is evaporating until it is dry. The fractionation between water and vapor, $\varepsilon^{18}O_{w-v}$ is 9.3‰ (Table 2-7), which means that the vapor being produced is 9.3‰ depleted in $^{18}O$ than the water from which it is evaporating. If the original $\delta^{18}O$ of the water is –10‰, then the vapor will initially have $\delta^{18}O$ = –19.3‰. This depletion in the product reservoir means that there is a gradual accumulation of $^{18}O$ in the reacting reservoir – the pond. This process is a Rayleigh distillation, represented by the general equation:

$$R_f = R_o\, f^{(\alpha-1)}$$

where $R_f$ is the isotope ratio of the reactant reservoir (the pond) after partial reaction (evaporation) to form the product (vapor) and leaving a residual fraction, $f$, in the pond. $R_o$ is the initial isotopic ratio of the reactant reservoir when $f = 1$ (when the pond was full).

For the example of $^{18}O$ in evaporation of water, this would be:

$$\left(\frac{^{18}O}{^{16}O}\right)_{water} = \left(\frac{^{18}O}{^{16}O}\right)_{initial\ water} f^{\left(\alpha_{vapor-water}-1\right)}$$

Note that the equilibrium fractionation factor is written in the form of the product over the reactant – $\alpha_{prod-react,}$ just like the mass action constant, K. A simplification of the Rayleigh equation is used in order to express isotope ratios in $\delta$–‰ notation and the fractionation factor in $\varepsilon$–‰ notation. Converting the isotope ratios to $\delta$ values gives:

$$\delta_{react} = \delta_{initial\ react} + \varepsilon_{prod-react} \cdot \ln f_{residual\ react} \qquad\qquad \delta^{18}O_{water} = \delta^{18}O_{initial\ water} + \varepsilon^{18}O_{vapor-water} \cdot \ln f$$

Plotting this relationship for the residual water in the evaporating pond gives the exponential curve in Fig. 2-13. The key observation in such a Rayleigh distillation is the extreme isotopic value that can be reached in the reactant reservoir. When the residual water has been reduced to a small fraction of its original volume, its $\delta^{18}O$ composition becomes greatly enriched due to the discrimination against $^{18}O$ during reaction (evaporation). In fact, evaporation is a non-equilibrium process as it takes place under conditions of low humidity (kinetic reaction). The enrichment factors for $^{18}O$ and D during evaporation are greater than the equilibrium values given in Table 2-7, and become even greater with decreasing humidity.

This extreme depletion (or enrichment, depending on whether $\varepsilon$ is positive or negative) is characteristic of Rayleigh distillation reactions. Other examples include the freezing of water in limited volumes of surface water (ponds, frost blisters), and geochemical reactions such as sulfate reduction or methanogenesis (see Chapter 6). One of the most important examples, however, is the partitioning of $^{18}O$ and D through the hydrological cycle. This is essentially driven by the Rayleigh distillation of isotopes from vapor masses as they cool and rain-out over the continents. This is why tropical rains are enriched in $^{18}O$ and D, while the

rain and snow of cold climate regions is highly depleted. This Rayleigh distillation of isotopes during rain-out is the process that partitions isotopes throughout the meteorological cycle and provides a versatile tracer of meteoric waters.
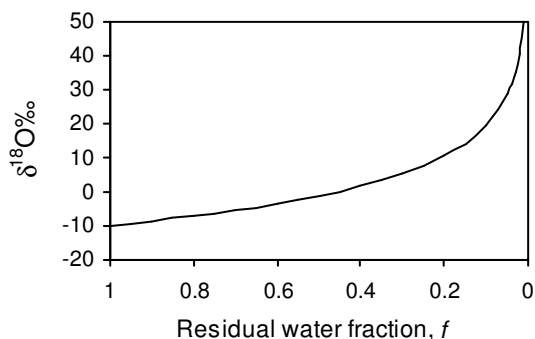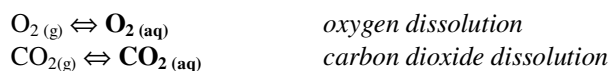


Fig. 2-13   Rayleigh distillation of $^{18}O$ in water during evaporation of a pond. The initial $\delta^{18}O$ of the pond water is $-10‰$. This becomes gradually enriched as $^{18}O$ accumulates in the residual water as water vapor is formed. Normally, evaporation is a non-equilibrium process and so the enrichment factor, $\varepsilon^{18}O_{vapor-water}$ is greater than the equilibrium value of $-9.3‰$ used in this graph.
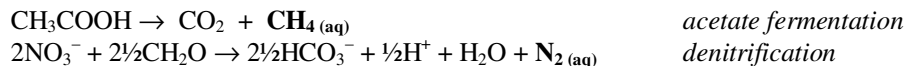
## GAS DISSOLUTION REACTIONS

An important component of aqueous geochemistry is the reactions of gases in water. Atmospheric $O_2$ plays a critical role in the oxidation of minerals such as pyrite, or organic matter. $CO_2$ dissolved from soils by infiltrating groundwaters provides carbonic acid for weathering reactions. Noble gases are non-reactive, and so are useful tracers due to the dependence of their solubilities on temperature. Other gases such as $CH_4$ and $N_2$ are produced as a product of bacterial activity in groundwaters and reflect in-situ geochemical conditions.
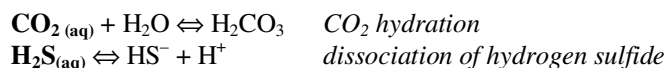
Gas dissolution reactions can involve the diffusion of the gas molecule through the gas – water interface, where it becomes an aqueous species:

$$O_{2\,(g)} \Leftrightarrow \mathbf{O_{2\,(aq)}} \qquad \textit{oxygen dissolution}$$
$$CO_{2(g)} \Leftrightarrow \mathbf{CO_{2\,(aq)}} \qquad \textit{carbon dioxide dissolution}$$

By contrast, they can be produced in groundwater by geochemical reaction:

$$CH_3COOH \rightarrow CO_2 + \mathbf{CH_{4\,(aq)}} \qquad \textit{acetate fermentation}$$
$$2NO_3^- + 2\tfrac{1}{2}CH_2O \rightarrow 2\tfrac{1}{2}HCO_3^- + \tfrac{1}{2}H^+ + H_2O + \mathbf{N_{2\,(aq)}} \qquad \textit{denitrification}$$

Some dissolved gases can react with water, such as the hydration of $CO_2$ to form carbonic acid, or the dissociation of hydrogen sulfide:

$$\mathbf{CO_{2\,(aq)}} + H_2O \Leftrightarrow H_2CO_3 \qquad \textit{CO$_2$ hydration}$$
$$\mathbf{H_2S_{(aq)}} \Leftrightarrow HS^- + H^+ \qquad \textit{dissociation of hydrogen sulfide}$$

The solubility of gases in water has more to do with physics and the gas law than with formal aqueous chemistry. This is presented in more detail, with calculations of the partial pressure of dissolved gases, in the next section.

### Concentrations of dissolved gases

While gases tend to partition into gaseous phases (notably our atmosphere) they are also found dissolved in water as un-ionized solutes. Gases are also found within minerals and rocks trapped in fluid inclusions and between mineral lattices. Gas solubilities in water are proportional to pressure, as opening a bottle of beer demonstrates. Gases from the atmosphere dissolved in surface water to the point of saturation at a pressure of one atmosphere. However, at greater depth below the lake surface or water table, the pressure is greater and the water becomes undersaturated with its dissolved gases, i.e. it could take more into solution. Scuba divers know about this, as breathing compressed air at depth allows more $N_2$ to dissolve into the blood, and must be allowed to diffuse out before surfacing to prevent formation of $N_2$ bubbles. The equilibrium concentration of an individual gas in water is a function of its solubility and pressure. Because gases are not ionized, we can consider their activity coefficients to be equal to 1 for most low salinity waters and so work with concentrations, $C_{gas}$, rather than activities.

For an ideal gas in a mixture of gases, its concentration is equal to its molar fraction, a unit-less ratio equal to the moles of the gas in question to the moles of all the gases in a given volume. For abundant gases in the atmosphere, concentration is expressed as a percent of the total gas ($N_2$ and $O_2$; Table 2-8). For gases of low to trace concentration, they are usually expressed as ppmv or ppbv — parts per million or billion by *volume*. This expression differs from the ppm used for solutes which is parts per million by weight, and assumes that the gases behave ideally, with no interaction.

The partial pressure of a gas, $P_{gas}$ is its fractional contribution to the total gas pressure $P_{total}$, and is calculated as its molar fraction multiplied by the total gas pressure:

$$P_{gas} = \frac{mols_{gas}}{mols_{total}} \cdot P_{total} \quad (atm)$$

Note that some publications express partial pressures of gases as pGas (i.e. $pO_2$), despite that this notation is taken to express a negative log (i.e. pH, pK, and p$e$). Gas pressure is commonly expressed in units of atmospheres (atm) although bars and kilopascals can also be used (1 atm = 1.01325 bar = 101.325 kPa). For example, $O_2$ in air has a molar fraction (or mixing ratio) of 0.209 or about 21% (Table 2-8), and at the Earth's surface has a partial pressure, $P_{O_2} = 0.21$ atm. At an altitude of 10 km, however, it has the same molar fraction but a partial pressure of only 0.18 atm. Carbon dioxide has a concentration in air of 370 ppmv or a molar fraction of 0.00037. At 1 atm total pressure, $P_{CO_2} = 0.00037$ or $10^{-3.43}$ atm. Taking an aliquot of the atmosphere and doubling its pressure (compressing its volume to half) will not change the molar fraction of these gases, but it will double their partial pressures.

For aqueous solutions, Henry's Law holds that the activity (or solubility) of a gas in pure water is proportional to its partial pressure in the adjacent gas phase. Henry's constant — $K_H$ is a measure of the solubility of a gas, expressed as molality, $m$ — moles of gas per kg $H_2O$:

$$K_{H\,gas} = \frac{m_{gas}}{P_{gas}} \qquad \text{Henry's Law constant}$$

As the partial pressure for the gas, $P_{gas}$, is in atmospheres, the units of $K_{H\,gas}$ are mol/kg/atm or $m$/atm. Table 2-8 gives $K_H$ for the common atmospheric gases, which are plotted in Fig. 2-14 according to their atomic mass. Note that solubility goes up with increasing atomic mass (Fig. 2-14), although there are anomalies. High solubilities for some gases reflect their reactivity with water. $CO_2$ is the most reactive, as it readily hydrates to form carbonic acid — $H_2CO_3$.

For example, the solubility of $O_2$ is defined by the Henry's Law constant (at 25°):

$$K_{O_2} = 10^{-2.89} = \frac{m_{O_2(aq)}}{P_{O_2}}$$

Thus, freshwater in equilibrium with the atmosphere ($P_{O_2}$ = 0.21 atm or $10^{-0.68}$) at 25°C would have dissolved oxygen (DO) concentration of $O_{2\ (aq)}$ equal to 0.253 mmol/L or 8.1 mg/L.

Table 2-8    Common atmospheric gases, their Henry's Law constants and Bunsen coefficients at 25°C and their aqueous solubility when at equilibrium with the atmosphere (Sander, 1999; Smith and Kennedy, 1983).

| Gas | gfw | Partial pressure P(atm) | Molar fraction in air | | $K_H$ mol/L/atm | Atmospheric Equlibrium (ppm) | Bunsen coefficient $(cc_{STP}/cc/atm)^1$ | Atmospheric Equilibrium $(cc_{STP}/cc)^1$ |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| $N_2$ | 28 | 0.78084 | 78.10 | % | 0.00065 | 14.2 | 0.01457 | 1.14E-02 |
| $O_2$ | 32 | 0.209476 | 20.90 | % | 0.0013 | 8.71 | 0.02914 | 6.10E-03 |
| Ar | 39.9 | 0.00934 | 0.93 | % | 0.0014 | 0.522 | 0.03130 | 2.92E-04 |
| $CO_2$ | 44 | 0.00037 | 370 | ppmv | 0.034 | 0.570 | 0.78449 | 2.90E-04 |
| Ne | 20.2 | 1.82E-05 | 18.2 | ppmv | 0.00045 | 1.65E–04 | 0.01024 | 1.86E-07 |
| He | 4 | 5.24E-06 | 5.24 | ppmv | 0.00038 | 7.96E–06 | 0.00876 | 4.59E-08 |
| $CH_4$ | 16 | 1.80E-06 | 1.8 | ppmv | 0.0014 | 4.03E–05 | 0.03138 | 5.65E-08 |
| Kr | 83.8 | 1.14E-06 | 1.14 | ppmv | 0.0025 | 2.39E–04 | 0.05620 | 6.41E-08 |
| $H_2$ | 2 | 5.00E-07 | 0.5 | ppmv | 0.00078 | 7.80E–07 | 0.01748 | 8.74E-09 |
| $N_2O$ | 44 | 2.50E-07 | 0.25 | ppmv | 0.025 | 2.75E–04 | 0.56035 | 1.40E-07 |
| Xe | 131.3 | 8.60E-08 | 0.086 | ppmv | 0.0043 | 4.86E–05 | 0.09810 | 8.44E-09 |
| $SO_2$ | 64 | 7.00E-09 | 0.007 | ppmv | 1.4 | 6.28E–04 | 31.37980 | 2.20E-07 |

[1] cc gas at STP per cc water. STP = standard temperature and pressure (273.15K or 0°C and 1 atm. pressure).

Problem: What would be the concentrations of $N_2$ and $CO_2$ in freshwater that has equilibrated with the atmosphere?        - - - - TO BE DEVELOPED - - - - -

Reformulating Henry's Law and using the constants for $N_2$ ($K_{H\ N2}$ =  0.00065) and $CO_2$ (KH CO2 = 0.035)

$$m_{N2} = K_{H\ N2} \text{ x } P_{N2}$$

While concentrations of gases in water can be expressed as mole fractions, they can also be expressed volumetrically. This is most common with the noble gases, which are non-reactive under all conditions and so are measured volumetrically. At standard temperature and pressure (STP), one mole of gas occupies 22.414 liters. Thus, an amount of gas (moles) in a given volume can be determined through the gas law:

$$PV = nRT \qquad \text{or} \quad n = \frac{PV}{RT}$$

where n is the number of moles of the gas, P is pressure (atmospheres), V is volume (L, cm$^3$ or cubic cm — cc), R is the gas constant (0.082058 atm L mol$^{-1}$ K$^{-1}$ or 8.3143 J/mol/K) and T is absolute temperature (K). For one mole of gas at one atmosphere pressure and 273.15K (STP), its volume V = RT = 22.414 L.

This leads to the expression of gas concentration, particularly for the noble gases, as cc$_{gas}$ at STP per cc water, or is per one cubic centimeter of water (cc or 1 ml). The solubility constant is no longer the Henry's Law constant (moles per liter per atmosphere or *M*/atm) but the Bunsen coefficient, B. From the gas law, Bunsen coefficient is simply the Henry's Law constant multiplied by RT:

Henry's Law constant $\qquad K_H = \text{mols/L} = \text{n/L}$

Gas law $\qquad\qquad\qquad n = \dfrac{PV}{RT} = RT$ for 1 L and 1 atm pressure.

Bunsen coefficient: $\qquad B = K_H RT \qquad (L_{STP}/L_{H_2O}/atm$ or $cc_{STP}/cc/atm)$
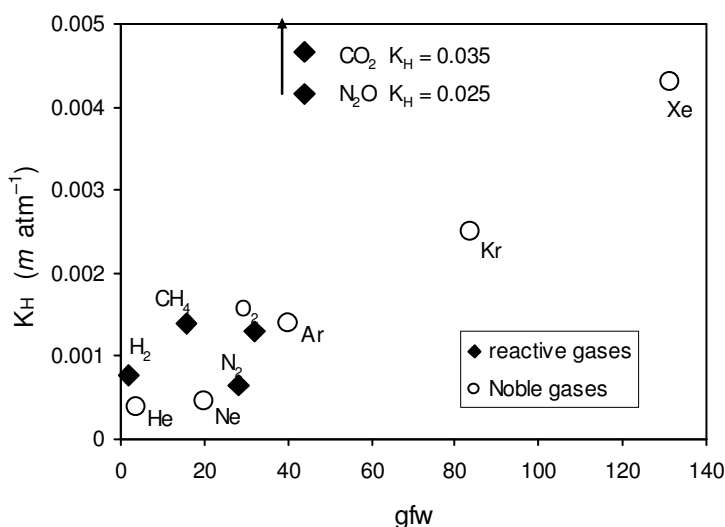


Fig. 2-14    The solubility of common atmospheric gases according to their atomic mass (gfw) at 25°C. Note that the solubility increases with atomic mass due to the lower kinetic energy (lower diffusion) of the larger gas molecules. It also increases with reactivity in water. The most reactive gases, $CO_2$ and $N_2O$ have very high solubilities in water (high $K_H$ values).


### *Effects of temperature and salinity*

Just as opening a beer demonstrates the solubility of gases with pressure, drinking warm beer demonstrates the decreasing solubility of gas with temperature. Increased temperature increases the kinetic energy of the un-ionized gas molecules and so decreases their capacity to be retained in the aqueous phase.

Add equations for temperature solubility.

A final analogy with beer illustrates the decreased solubility of gas with increased salinity, as demonstrated by sprinkling salt into a glass of beer. The salt grains act as nucleation points for bubbles to form, but they also increase the salinity, thereby decreasing the equilibrium partial pressure of the dissolved $CO_2$.

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## PROBLEMS

Dissociation Reactions

1.  Write out the reactions for the dissolution of fluorite and for the hydrolysis of $Fe^{3+}$, and the equation for the law of mass action for each.

2.  Write balanced equations for the following aqueous reactions:

    (i)       hydration of $CO_2$ and dissociation of carbonic acid

    (ii)      dissolution of dolomite with $CO_2$ in water

    (iii)     precipitation of ferrihydrite from waters with dissolved $Fe^{3+}$.

    (iv)      dissolution of gypsum and precipitation of barite in a $Ca^{2+}$-$Ba^{2+}$-$SO_4^{2-}$ solution.

3.  Calculate the ionic strength of a 0.05 molal $Na_2SO_4$ solution, ignoring the effects of complex ions.
    What are the activities of $Na^+$ and of $SO_4^{2-}$?
    What would be the effect of any complex ions such as $NaSO_4^-$ on the ionic strength and on your calculated activities of $Na^+$ and $SO_4^{2-}$.

4.  The following analysis comes from groundwater collected during a pump test for a newly drilled water well. Will there be a problem with mineral precipitation in the plumbing?  (concentrations in ppm):

    | | | | |
    |---|---|---|---|
    | Temperature | 25°C | pH | 7.95 |
    | $Ca^{2+}$ | 30 | $HCO_3^-$ | 120 |
    | $Mg^{2+}$ | 4 | $CO_3^{2-}$ | 0.49 |
    | $Na^+$ | 10 | $SO_4^{2-}$ | 2 |
    | $K^+$ | 2 | $Cl^-$ | 12 |

5.  For the following groundwater analyses (concentrations in mg/L):

    | | T | pH | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Sr^{2+}$ | $HCO_3^-$ | $CO_3^{2-}$ | $SO_4^{2-}$ | $Cl^-$ |
    |---|---|---|---|---|---|---|---|---|---|---|---|
    | GW1 | 25 | 7.54 | 205 | 11 | 33 | 16 | 0.01 | 380 | 0.61 | 25 | 111 |
    | GW2 | 25 | 7.40 | 120 | 15 | 380 | 22 | 0.8 | 150 | 0.10 | 1115 | 15 |

    Determine:   - meq/L for all cations and anions
                 - the charge balance. Is this an acceptable analysis?
                 - the ionic strength, $I$
                 - the activity co-efficients and activities for all ions using the extended Debye-Hückel

6.  Using the data in Table 2-4, calculate the solubility products, Ksp for anhydrite and celestite. What are the states of saturation of these minerals for the GW2 waters in the above question?

7.  Fluoride — $F^-$ is a contaminant in groundwater at concentrations greater than 1 mg/L. What is the concentration of $F^-$ in a groundwater, which dissolves fluorite — $CaF_2$, to the point of saturation? Now determine the concentration of $F^-$ when the groundwater first reaches equilibrium with gypsum, then begins to dissolve fluorite? Assume activities equal molalities.

8.  In Example 2-4, we calculated that 0.011 mol/kg of gypsum can be dissolved in pure water. The effects of complex species were not taken into account. Using the geochemical speciation program WATEQ, determine the state of saturation for gypsum in a 0.011 $m$ $Ca^{2+}$ – $SO_4^{2-}$ solution.

9.  Use WATEQ to determine the speciation for the geochemical analysis of GW1 and GW2 in question 5 above.
    (i)     How do the WATEQ saturation indices for calcite, gypsum and dolomite differ from the hand calculations in question 3. Suggest reasons why they may differ?

    (ii)    What are the $P_{CO_2}$ values for GW1 and GW2? Are they greater or less than the atmospheric value (currently we have 370 ppmv $CO_2$).

### *Redox reactions:*

10. Write the two redox half reactions that define the upper and lower stability limits for water.

11. Provide an example of electron donor and electron acceptor species (redox couple) for S, N, Fe and As, and write balanced redox half-reactions for the electron transfer.

12. Write the two complementary redox half-reactions for (i) the oxidation of hydrogen — $H_2$ by $O_2$ and (ii) oxidation of methane — $CH_4$, with $O_2$. Determine the Gibb's free energy for each overall reaction. Which would provide more energy to bacteria, per mole of $O_2$ consumed?

13. What would be the measured Eh of a solution with pH = 7 that contained equal activities of $H_2S$ and $SO_4^{2-}$? (hint: begin by finding the p$e$ of the redox half reaction for sulphate reduction)

### *Isotope Fractionation Reactions:*

14. Atmospheric water vapor is seldom sampled and measured for isotopes, but assume that for a given time and place it is found to have a $\delta^{18}O$ value of –18‰. What would be the $\delta^{18}O$ value for rain that fell with a condensation temperature of 15°C?

15. Write an example of an equilibrium isotope exchange reaction involving each of the isotopes and associated samples in Table 1-4.

16. The analysis of $^{18}O$ in water is done by equilibrating the sample with $CO_2$ and then measuring $\delta^{18}O_{CO_2}$. The fractionation factor for this exchange of $^{18}O$ between $CO_2$ and $H_2O$ is $\alpha^{18}O_{CO_2-H_2O}$ = 1.0415 at 25°C (and so $\varepsilon^{18}O_{CO_2-H_2O} = (\alpha–1) \cdot 1000$). For $\delta^{18}O_{CO_2}$ measurements of +35.5‰ and +32.1‰ VPDB (samples A and B), what are the values for $\delta^{18}O_{H_2O}$ for A and B?

17. The enrichment factor for isotopes, $\alpha$, particularly for kinetic reactions, can be calculated from isotope measurements of the two reacting phases, such as for, or $^{18}O$ in water and evaporated vapor. Determine

the fractionation factor, $\alpha$, and the enrichment factor, $\varepsilon$, for the following two isotope exchange reactions (hint: first derive the fractionation factor, $\alpha$ in terms of $\delta$ values).

- $^{18}O$ during strong evaporation under low humidity conditions, $H_2O_{water} \rightarrow H_2O_{vapor}$
  $$\delta^{18}O_{water} = -10‰ \quad \text{and} \quad \delta^{18}O_{wapor} = -25‰$$
- $^{13}C$ during photosynthesis: $CO_2 + H_2O \rightarrow CH_2O + O_2$
  $$\delta^{13}C_{CO_2} = -8‰ \quad \text{and} \quad \delta^{13}C_{CH_2O} = -26‰$$

18. A pond of water, with $\delta^{18}O = -10‰$ starts to evaporate to dryness. Given an enrichment factor for isotope exchange between water and vapor of $\varepsilon^{18}O_{vapor-water} = -9.3‰$, $(\alpha^{18}O_{water-vapor} = 1.0093)$ determine the isotopic composition of the pond water when it has evaporated to residual fractions $f = 0.5$, $f = 0.15$, $f = 0.05$ and $f = 0.01$. What would be the effect on your calculations if you used a kinetic enrichment factor which was less than $-9.3‰$ (say $-13‰$).

19. A sample of water in a partially filled container has a $\delta^{18}O$ value of $-7.0‰$. The temperature is $25°C$. What will be the $\delta^{18}O$ value of the water vapor in isotopic equilibrium with this water?

20. What are the $^{18}O$ fractionation factors and the $^{18}O$ enrichment factors for water in equilibrium with vapor at $0°C$ and at $50°C$? At which temperature will there be a greater difference between measurements of $\delta^{18}O_{water}$ and $\delta^{18}O_{vapor}$, and what are the differences?

21. Write the fractionation factor, $\alpha^{18}O_{water-vapor}$ in terms of an isotope ratio for these compounds.

20. A small lake was profiled for dissolved oxygen (DO as $O_2$) as well as for temperature and pH. Calculate the percent saturation for DO at each measurement depth. (Note that Henry's constant at different temperatures can be calculated from: $K_{H-O_2} = 5E\text{-}07\ T^2 - 5E\text{-}05\ T + 0.0022$).

With reference to the pH, account for the anomaly at 2 m depth and the decrease in DO below this depth.

| Depth (m) | Temp (Celsius) | DO (mg/L) | Cond ms/cm | pH |
|---|---|---|---|---|
| 0.5 | 23.70 | 6.82 | 320 | 8.23 |
| 1.0 | 23.53 | 6.80 | 319 | 8.13 |
| 1.5 | 22.12 | 9.92 | 332 | 7.88 |
| 2.0 | 18.12 | 18.20 | 334 | 9.16 |
| 2.5 | 14.29 | 1.29 | 345 | 7.32 |
| 3.0 | 9.85 | 0.82 | 348 | 6.85 |
| 3.5 | 7.24 | 0.70 | 347 | 6.68 |
| 4.0 | 5.90 | 0.62 | 348 | 6.57 |
| 4.5 | 4.92 | 0.53 | 354 | 6.47 |
| 5.0 | 4.41 | 0.46 | 358 | 6.41 |
| 5.5 | 4.15 | 0.39 | 368 | 6.30 |