
WATER AND SOLUTIONS

Soil chemistry centers around the soil solution, the aqueous solution that reacts with, and is between, the solid phase and roots and soil microbes. A *solution* is defined as a mixture and usually means an *aqueous solution*—a mixture of solutes and water. Soil and rock minerals can be considered *solid solutions*, because they contain foreign ions that are mixed into the mineral's structure. Soil chemistry involves both aqueous and solid solutions. This chapter presents the chemistry of ions reacting with H^+ , OH^- , O^{2-} , and H_2O in the soil solution and soil minerals.

The state of ions in aqueous solution is similar to their states in soil minerals and solid solutions because both water and soil minerals are dominated by the O^{2-} ion. Water is an oxide whose charge is countered by H^+ . In minerals the O^{2-} charge is countered by many other cations. Water reacts somewhat like O^{2-} with cations, but much more weakly. The solute composition of the soil solution is the result of competition of the oxide groups in soil solids with H^+ , OH^- , and H_2O in the soil solution.

Water molecules also interact with each other. The interaction is indicated by water's relatively high boiling point and specific heat (the amount of energy needed to raise its temperature). The H_2O molecule as written looks similar to H_2S , and water should boil at a lower temperature because oxygen has a lower atomic weight than sulfur. However, H_2S boils at a much lower temperature, $-61^\circ C$, than water at $0^\circ C$, because the H_2S molecules are much more independent and interact very weakly. The H^+ ions in H_2S are 180° apart, creating a linear, *nonpolar* molecule. The H^+ ions in H_2O are 105° apart, creating a nonlinear, *polar* molecule. This is a *dipole* with positive (the hydrogen side) end and a negative (the side opposite the H ions) end. Technically, water is a quadrupole but that sophistication is unnecessary here. The positive end of one water molecule attracts the negative end of another

water molecule. This electrostatic attraction is absent in the nonpolar H_2S molecule, which has no positive and negative ends. Water molecules cluster together in groups averaging about six in number at room temperature. Because of thermal motion, the groups continually break apart and reform. In ice the structure is a rigid, open hexagonal packing of water molecules. In water, the small groups are thought to have a similar structure, but each group is not oriented to the next group. The groups can slide closer together so water is denser than ice. Water is like an ice slurry on a molecular scale.

Ions and charged surfaces can break down the “ice slurry” structure of water. The electric charges are stronger than dipole forces and tend to pull water molecules away from their groups by attracting the positive or negative ends of the water dipoles. Solutes and water molecules are constantly in motion, but they remain in the vicinity of each other for some period of time. If water molecules remain near an ion longer than the time required for the water molecules to dissociate from the water structure, the ion will have a sphere of water molecules (a *solvation sphere* or *sheath*) around itself. The number of water molecules in the closest solvation sphere is called the *primary hydration number*.

The value of the primary hydration number is in dispute. Different methods of measurement yield quite different values because they respond to different strengths and times of ion–water interaction. Careful measurements of the hydration number of Na^+ , for example, yielded values of 1, 2, 2.5, 4.5, 6 to 7, 16.9, 44.5, and 71, depending on the method used. Table 3.1 shows hydration numbers for common ions determined by several methods that tend to agree. The last column shows Bockris and Reddy’s estimates of primary hydration numbers for the univalent ions.

Outside of the primary solvation sphere is a second sphere of water molecules also affected by the ion’s charge. These water molecules have also been torn away from their water structure to some extent, but are not so closely associated with the ion. The orientation of water molecules in the primary solvation sphere and the more random orientation of water molecules in the secondary sphere essentially dissipate

Table 3.1. Primary hydration numbers

	From ion compressibility	From thermodynamic calculations	Most probable value
Li^+	5–6	5	5 ± 1
Na^+	6–7	4	4 ± 1
K^+	6–7	3	3 ± 2
F^-	2	5	4 ± 1
Cl^-	0–1	3	2 ± 1
Br^-	0	2	2 ± 1
I^-	0	1	1 ± 1

Table 3.2. Crystallographic radii and heats and entropies of ion hydration at 25° C

Ion	Crystallographic Ion Radius (nm)	Heat of Hydration, ΔH (kJ mol ⁻¹)	Entropy of Hydration, ΔS (J mol ⁻¹ K ⁻¹)
H ⁺	—	-1090	109
Li ⁺	0.060	-506	117
Na ⁺	0.095	-397	87.4
K ⁺	0.133	-314	51.9
Rb ⁺	0.148	-289	40.2
Cs ⁺	0.169	-255	36.8
Be ²⁺	0.031	-2470	—
Mg ²⁺	0.065	-1910	268
Ca ²⁺	0.099	-1580	209
Ba ²⁺	0.135	-1290	159
Mn ²⁺	0.080	-1830	243
Fe ²⁺	0.076	-1910	272
Cd ²⁺	0.097	-1790	230
Hg ²⁺	0.110	-1780	180
Pb ²⁺	0.120	-1460	155
Al ³⁺	0.050	-4640	464
Fe ³⁺	0.064	-4360	460
La ³⁺	0.115	-3260	368
F ⁻	0.136	-506	151
Cl ⁻	0.181	-377	98.3
Br ⁻	0.195	-343	82.8
I ⁻	0.216	-297	59.8
S ²⁻	0.184	-1380	130

the ion's charge within 1 to 2 nm of the central ion. This charge dissipation allows the ions to interact less electrostatically with each other.

The degree of breakdown of the water structure, plus the degree of formation of new ion- or solute-water structures, is measured by the heat of hydration (Table 3.2). Heats of hydration are less ambiguous than structural concepts of hydration numbers and ion-, solute-, or clay-water interactions.

The heat of hydration increases negatively, indicating increased interaction, with decreasing ion size for a given valence group, from -506 kJ mol⁻¹ for Li⁺, atomic number 7, to -255 kJ mol⁻¹ for Cs⁺, atomic number 133. The heat of hydration also increases negatively with increasing ionic charge. The heat of hydration for monovalent cations is several hundred kJ mol⁻¹; for divalent cations, it is about -1600 kJ mol⁻¹; and for trivalent cations, it is about -4000 kJ mol⁻¹.

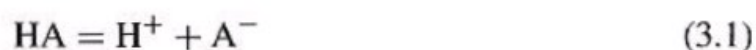
The highly negative heats of hydration for the trivalent ions support the idea that they exist as Fe(H₂O)₆³⁺ and Al(H₂O)₆³⁺ (hexaquoiron(III) and hexaquoaluminium) ions in water. The ion and water molecules in such complexes are tightly bound and

together behave like a single large ion. Divalent transition metal ions and Mg^{2+} form similar but weaker structures with water. The other alkaline earth cations are larger and associate less strongly with water.

Soil particle surfaces are also charged so they attract ions and water dipoles. The charge can be an atomic layer beneath the crystal surface so the interaction between soil particles and water is weaker than between ions and water. At the edges of crystals, the charge is weaker but at the surface.

3.1 ACIDS AND BASES

Substances that liberate H^+ in solution are *Bronsted acids*. Strong acids like HCl, HNO_3 , $HClO_4$, and H_2SO_4 completely dissociate into H^+ (which probably exists as the hydrated or *hydronium* ions H_3O^+ or $H_7O_3^+$) and an anion. Weak acids deprotonate less readily. Examples are Al^{3+} ($pK_1 = 5$), HF ($pK = 3.2$), and organic acids such as acetic acid, CH_3COOH ($pK = 5$), where K is the dissociation constant of the acids. Their more tightly bound protons dissociate at higher pH than strong acids. For the generalized weak acid HA,



and its dissociation, deprotonation, or acidity constant is

$$K_{HA} = \frac{(H^+)(A^-)}{HA} \quad (3.2)$$

Just as acids differ in strength, bases similarly differ in their ability to give up hydroxyl ions. The strong bases NaOH and KOH dissociate completely in solution. Bases such as $Ca(OH)_2$ and $Mg(OH)_2$ are only slightly less dissociated in solution, but are considerably less soluble than either NaOH or KOH. This lower solubility accounts for the lower pH of $Ca(OH)_2$ and $Mg(OH)_2$ solutions more accurately than does weak dissociation.

Weak bases are more precisely compounds like NH_4OH ($pK_b = 5$), where pK_b is the negative log of the equilibrium constant:

$$K_{NH_4OH} = \frac{(NH_4^+)(OH^-)}{NH_4OH} = 10^{-5} \quad (3.3)$$

The NH_4OH molecule is the hydrate of NH_3 , which is very soluble in water. Most of the solute remains in solution as NH_3 , but a small portion forms NH_4OH , which dissociates into NH_4^+ and OH^- . The denominator of Eq. 3.3 is really the sum of the dissolved NH_3 plus NH_4OH . Dissolved CO_2 and H_2CO_3 are identical with ammonia in this respect.

Because the pH change during titration of acid soils with OH^- resembles the titration curves of weak acids with OH^- , soil clays were called weak acids for many years. For two main reasons, however, weak acid inadequately describes soil acidity.

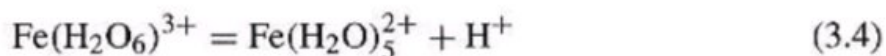
Firstly, soil acidity changes slowly with time after liming, for example, while true weak acids react instantly with OH^- . Freshly prepared acid clays are strongly acidic but begin to decompose to weak acids within a few hours. The clay decomposition liberates Al^{3+} . The base added to the decomposed acid clay actually titrates Al^{3+} , which has a titration curve resembling that of a weak acid. Aluminium hydrolysis and clay decomposition are slow, however, so the suspension pH changes slowly with time. Secondly, the amount of soil acidity released depends on the salt concentration of the bulk solution, but salt concentration has little effect on true weak acids. The term weak acid is better restricted to those compounds whose acidity is independent of time and salt concentration, such as acetic acid and phosphoric acid. Soil organic matter satisfies the definition of a weak acid much better than do inorganic soil clays.

3.1.1 Hydrolysis and Deprotonation

The attraction of cations for water molecules is so strong that the cation's charge tends to repel hydrogen ions, or protons, from the water *ligands* in the solvation sphere and makes them Bronsted acids. As the solution is made more alkaline, more H^+ tends to dissociate. An example is phosphoric acid molecule formed by P^{5+} in solution, $\text{PO}(\text{OH})_3$, written more familiarly as H_3PO_4 . This molecule is stable in acid solutions. The +5 charge has already repelled 5 H ions from the four water molecules that originally surrounded P^{5+} . The first H^+ ion from H_3PO_4 is repelled by P^{5+} at about pH 3 to form H_2PO_4^- , the second at pH 7, and the last H^+ at pH 10.

The S^{6+} in sulfuric acid ($\text{SO}_2(\text{OH})_2$) and the N^{5+} in nitric acid (NO_2OH) are stronger acids, and the H^+ from these strong acids is repelled even in extremely acid solutions. The remnants of the water molecules in PO_4^{3-} , SO_4^{2-} , and NO_3^- are oxide (O^{2-}) ligands that are almost impossible to strip away from the central ion, unless the central ion is first reduced to a lower oxidation state.

A similar repulsion of H^+ occurs from the solvation sphere of hexaquoiron(III) ions,



This reaction is called *hydrolysis*, because it splits a water molecule, or *deprotonation*. The hydrolysis constant, ignoring the water ligands, is

$$K_{\text{H}} = \frac{(\text{H}^+)(\text{FeOH}^{2+})}{\text{Fe}^{3+}} = 10^{-2.2} \quad (3.5)$$

The $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ion is a weaker acid than sulfuric or nitric acid, but is a stronger acid than phosphoric acid. Table 3.3 gives the hydrolysis constants of several common cations. The smaller the hydrolysis constant (the more negative its exponent), the weaker the acid.

The hydrolysis of iron(III) continues progressively at still higher pH, giving

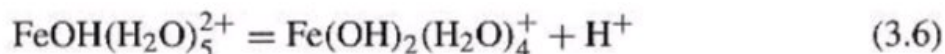


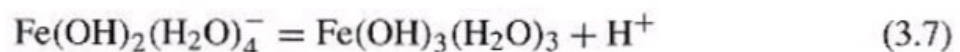
Table 3.3. Solubility products and hydrolysis constants of metal ions^a

Ion	log K_{sp}	log K_1^b	log K_2
Be ²⁺	-21	-6.5	
Mg ²⁺	-10.8	-12	
Ca ²⁺	-5.0	-12.5	
Mn ²⁺	-12.5	-10.5	
Fe ²⁺	-14.8	-7	
Ni ²⁺	-15	-8	
Cu ²⁺	-19.5	-7.5	
Zn ²⁺	-17	-9.1	
Cd ²⁺	-14	-10	
Hg ²⁺	-25.5	-3.5	
Pb ²⁺	-18	-8	
Al ³⁺	-33.5	-5	-5.5
Fe ³⁺	-39	-2.9	-3.3
La ³⁺	-20	-9	
Ti ⁴⁺ ((TiO ₂)(OH) ²)	-29	> -1	
Th ⁴⁺	-44	-4.1	

^aFrom L. G. Sillen and A. E. Martell, 1974. Stability constants. *The Chemical Society Spec. Publ.* 25, London.

$$^b K_1 = \frac{(\text{MOH}^{(n-1)+})(\text{H}^+)}{(\text{M}^{n+})}$$

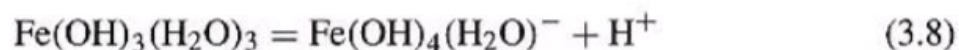
and



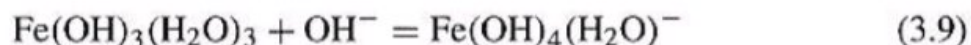
The uncharged $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3$ species does not repel other iron(III)-water ions and is therefore less water soluble than the charged ions. It can lose four water molecules and precipitate as FeOOH . FeOOH is more stable than $\text{Fe}(\text{OH})_3$. These hydrolysis reactions of iron and especially of aluminium are primary factors in the production and control of soil acidity.

The hydrolysis in Eqs. 3.4, 3.6, and 3.7 oversimplifies the actual mechanism of hydrolysis. The hydrolyzed ions begin to associate and form polynuclear ions, which enlarge with further hydrolysis. These polynuclear ions form in solutions and may exist in natural waters for a long time before they precipitate as a solid. Whether they exist in soil solutions, with the soil's large and adsorptive surface area and at the low concentrations in soil solutions, is less certain. When ions dissolve from solids, on the other hand, the ions formed most likely remain as mononuclear species because their concentrations are so low.

The hydroxyoxides are capable of still further hydrolysis if the pH becomes more alkaline. Iron hydroxide, for example, can dissolve according to the reaction



or



Equations 3.8 and 3.9 are equivalent, because producing 1 mol of H^+ is the same as consuming 1 mol of OH^- . The equilibrium constant is

$$K_h = \frac{\text{Fe}(\text{OH})_4^-}{\text{OH}^-} = 10^{-5.5} \quad (3.10)$$

The $\text{Fe}(\text{OH})_4^-$ ion, because it is charged, is more soluble than FeOOH . Hence, the solubility of $\text{Fe}(\text{III})$ increases at alkalinities above pH 8.5. Figure 3.1 shows the effect of pH on the distribution of aquohydroxyiron(III) species in solution.

The hydrolysis reactions of Al^{3+} are analogous to those of Fe^{3+} , but Al^{3+} is less acidic. The loss of the first H^+ from $\text{Al}(\text{H}_2\text{O})_6^{3+}$ occurs at pH 5. The hydrolysis of the second and third protons occurs at slightly higher pH and is complicated by polymerization of the hydrolysis products and slow precipitation of $\text{Al}(\text{OH})_3$. Figure 3.1

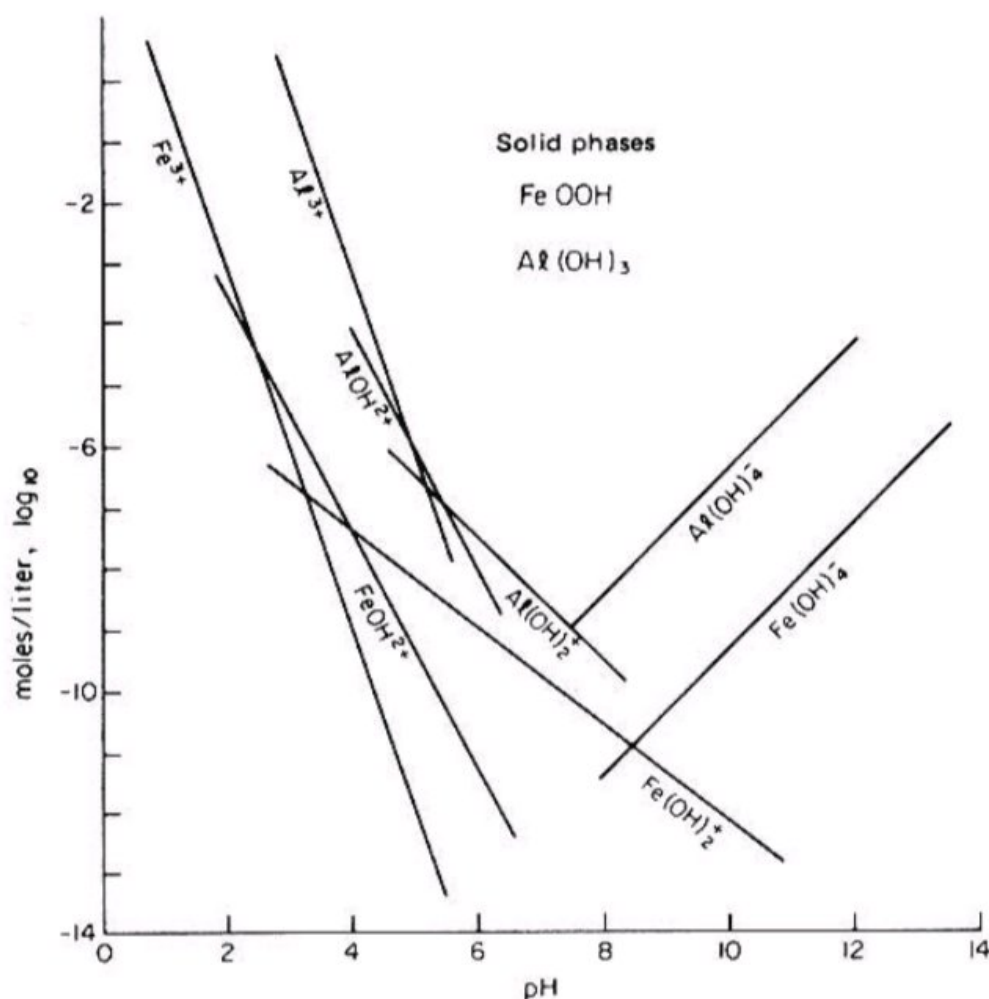


FIGURE 3.1. Equilibrium solubility of monomeric $\text{Fe}(\text{III})$ and $\text{Al}(\text{III})$ ions from FeOOH and $\text{Al}(\text{OH})_3$ as a function of pH.

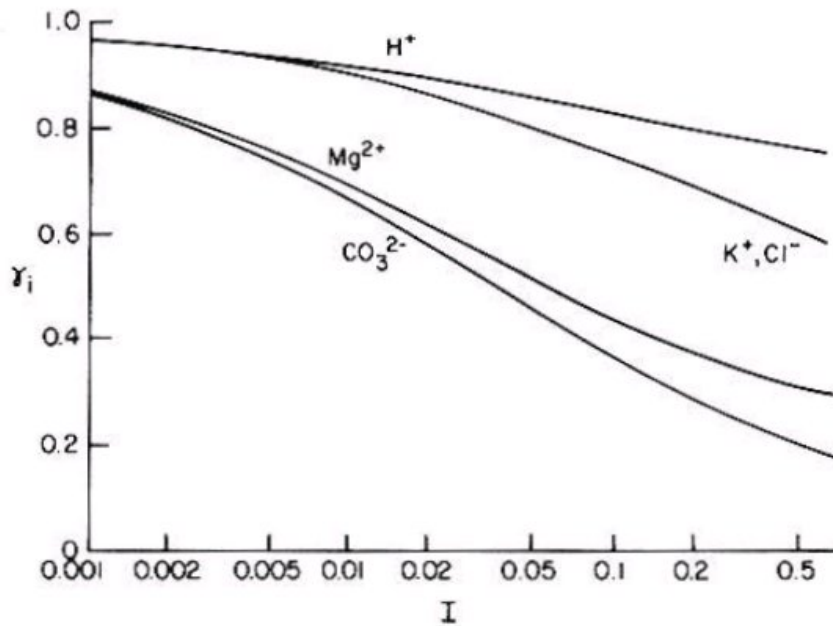


FIGURE 3.2. Ion activity coefficients versus ionic strength I . Calculated from the extended Debye–Hueckel equation.

disregards these complications. The $\text{Al}(\text{OH})_4^-$ begins to form above pH 8, but the exact value is uncertain.

High solubility in acidic and basic solutions, and low solubility at neutral pH, as shown in Figures 3.1 and 3.2, is called *amphoterism*. Amphoteric ions can form positive or negative hydroxy complexes depending on solution pH. This allows hydroxides to be both acidic and basic. $\text{Al}(\text{OH})_3$ consumes H^+ when dissolving in acid solutions, thereby acting like a base. By consuming OH^- and forming $\text{Al}(\text{OH})_4^-$, aluminium hydroxide acts like an acid. This amphoteric behavior is important to charge development by some soil clays.

The hydrolysis illustrated for Fe^{3+} and Al^{3+} can happen to all cations, but the extent of hydrolysis varies widely. Hydrated alkali and alkaline earth cations should deprotonate at extremely high pH, but sufficiently high pH values do not occur in nature. In typical soil solutions of pH 5 to 9, P(V) exists as H_2PO_4^- and HPO_4^{2-} in aqueous solutions, Fe(III) exists as $\text{Fe}(\text{OH})_2^+$, and Ti(IV) probably exists as $\text{TiO}(\text{OH})_2^{2-}$. Si(IV) in aqueous solution is $\text{Si}(\text{OH})_4$, also written H_4SiO_4 ; it loses its first H^+ only above pH 9. The pH values at which H^+ ions are lost from the solvation sheath are indicated by the negative logarithms of the hydrolysis constant, $\text{p}K$, and are shown in Table 3.3; $\text{p}K_h < 7$ indicates that the cations are acidic.

3.1.2 Solubility Products

Table 3.3 gives the solubility products of the metal hydroxyoxides that are likely to exist in soils. The general form of the solubility products is

$$K_{\text{sp}} = (\text{M}^{n+})(\text{OH}^-)^n \quad (3.11)$$

A solid also becomes less water soluble (the solubility product decreases) when its crystals are purer, their structure is more ordered, their size increases, and as the crystals contain less water (less hydrated), but these effects are secondary to the solubility product. The solubility product decreases as crystals grow in size and lose waters of hydration and occluded or coprecipitated ions. The slow growth and recrystallization is much more pronounced in the mixture of ions in soil solutions than in the pure aqueous solutions of the chemistry laboratory. The solid-phase reactions are often exceedingly slow in soils compared to the formation rates of new, poorly crystalline material. Hence, soil-formed crystals tend to be small and amorphous and to contain many impurities.

Solubility products measured in pure systems may not represent soil conditions very well. The impurities in solids affect their aqueous solubility; soil minerals are characteristically impure. Nonetheless, predictions of soil solution concentrations usually assume the solubility products of pure minerals apply. The water molecule is ignored in stability constant and solubility product equations. The concentration of water is assumed to be unity because water is present in great excess and does not change significantly during the reaction. This assumption is good in all but the most concentrated aqueous solutions and in dry soils.

3.2 CHEMICAL ACTIVITY

Ions in water are not free and unattached. They interact with water and with each other. Close-range (<0.5 nm) ion-ion interactions are termed *complex ions* or *ion pairs* and are governed by specific interactions between ions. These close-range interactions are discussed later. Longer-range (>0.5 nm) interactions are treated by the concept of chemical activity.

The interactions of ions with water molecules and other ions affect the concentration-dependent (*colligative*) properties of solutions. Colligative properties include osmotic pressure, boiling point elevation, freezing point depression, and the *chemical potential*, or *activity*, of the water and the ions. The activity is the driving force of reactions. Colligative properties and activities of solutions vary nonlinearly with concentration in the real world of nonideal solutions.

Solutes can be thought of as ideal by considering their activities rather than their concentrations. The activity is defined as

$$\alpha = \gamma M \quad (3.12)$$

where α is the activity, γ is the *activity coefficient*, and M is molarity. The activity can be regarded as an ideal concentration, but is more correctly defined as a ratio related to concentration and is unitless. The units of γ are then L mol^{-1} .

The colligative properties of an *ideal solution* are equal to the concentrations of the components, and their activity coefficients equal one. The deviation of the activity coefficient from one expresses the degree of nonideality. Figure 3.2 shows the change in the aqueous activity coefficients of several ions over the concentrations found in soil solutions and groundwater.

The activity coefficient is defined so that

$$\lim_{M \rightarrow 0} \gamma = 1 \quad (3.13)$$

As the concentration approaches zero, γ approaches one. As the solute is diluted by the solvent and the solute ions or molecules are farther apart, they interact less with each other and behave more ideally.

Water and ions are affected by the amounts and charges of all of the ions in the solution; the *ionic strength* I combines the effects of concentration and ion charge

$$I = \frac{1}{2} \sum M_i Z_i^2 \quad (3.14)$$

where M_i is the molarity, and Z_i is the charge, of each ion i . The ionic strength estimates the effective ion concentration by taking into account the large effect of ion charge on solution properties. A solution has only one ionic strength, but each ion may have a different activity coefficient (Fig. 3.2).

The properties of individual ions cannot be measured; we can only accurately measure the properties of salts and from them estimate the properties of ions. From a fundamental or thermodynamic standpoint, ions, therefore, do not exist, but we accept that they exist. We estimate the activities of ions by arbitrarily dividing up the activities of their salts. The activity of CaCl_2 in a CaCl_2 solution, for example, is

$$a_{\text{CaCl}_2} = \gamma_{\text{Ca}} \cdot M_{\text{Ca}^{2+}} (\gamma_{\text{Cl}} \cdot M_{\text{Cl}^-})^2 \quad (3.15)$$

remembering that the molarity of Cl^- is twice that of Ca^{2+} . The interaction between ions increases with concentration and with the square of the ion charge.

The activity of a salt can then be divided between cation and anion. By measuring the activities of NaCl , NaBr , NaNO_3 , and NaClO_4 , for example, the contribution of Na^+ to the total activity can be sorted out. This process is very laborious; calculating the ion activity directly would be much quicker.

Debye and Hueckel in 1924 proposed Eq. 3.16 using the ionic strength to account for the effect of all the ions in solution on the activity coefficient of ion i :

$$\log \gamma = -AZ_i^2 I^{1/2} \quad (3.16)$$

where γ is the ion's activity coefficient, A is a constant ($= 0.511$ for aqueous solutions at 25°C and is relatively insensitive to temperature), Z_i is the ion's charge, and I is the ionic strength. Equation 3.16 is called the Debye–Hueckel limiting law, because it predicts ion activity coefficients only in dilute solutions (solutions that have been cynically called “slightly contaminated distilled water”). Equation 3.16 was nonetheless a great breakthrough in the understanding of ion behavior in solutions.

Debye and Hueckel assumed that ions interact electrostatically like charged particles of zero size, but ions and their associated water molecules have significant physical size. These and other problems make Eq. 3.16 unreliable at ionic strengths greater than about 0.01. The equation has been modified to be useful up to $I = 0.1$:

$$\log \gamma = -AZ_i^2 \left(\frac{I^{1/2}}{1 + Ba_i I^{1/2}} \right) \quad (3.17)$$

where $B = 0.33$ for aqueous solutions at 25°C and a_i is an individual ion parameter determined experimentally. Table 3.4 gives a_i values for some common ions. Because values of a_i somewhat resemble the diameters of ions plus their associated water molecules, a_i is thought by some to have physical significance and has been termed the "distance of closest approach."

The empirical Davies equation

$$\log \gamma = AZ_i^2 \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right) \quad (3.18)$$

also yields satisfactory values for individual ion activity coefficients over the range of concentrations normally encountered in soil solutions and freshwaters.

Debye and Hueckel's work is historically important to soil chemistry because their derivation was similar to that of Guoy and Chapman, published independently about 1910, who tried to predict the ion distribution in the aqueous solution around a charged surface such as a soil particle. Although the Guoy–Chapman theory and its

Table 3.4. Values of a_i , the Debye–Hueckel "distance of closest approach"^a

INORGANIC IONS	a_i (10^{-9} m)
NH_4^+	0.25
Cl^- , NO_3^- , K^+	0.3
F^- , HS^- , OH^-	0.35
HCO_3^- , H_2PO_4^- , Na^+	0.4–0.45
HPO_4^{2-} , PO_4^{3-} , SO_4^{2-}	0.4
CO_3^{2-}	0.45
Cd^{2+} , Hg^{2+} , S^{2-}	0.5
Li^+ , Ca^{2+} , Cu^{2+} , Fe^{2+} , Mn^{2+} , Zn^{2+}	0.6
Be^{2+} , Mg^{2+}	0.8
H^+ , Al^{3+} , Fe^{3+} , La^{3+}	0.9
Th^{4+} , Zr^{4+}	1.1
ORGANIC IONS	
HCOO^-	0.35
CH_3COO^- , $(\text{COO})_2^{2-}$	0.45
Citrate ³⁻	0.5
$\text{C}_6\text{H}_5\text{COO}^-$	0.6

^aFrom J. Kielland. 1937. *J. Am. Chem. Soc.* 59:1675–1678.

later modification have shortcomings for soil–water systems, Debye–Hueckel successfully describes the less complicated conditions of dilute aqueous solutions.

Nonelectrolytes—dissolved gases, organic molecules, neutral ion pairs, and undissociated weak acids and bases—are also nonideal solutes in water and are common constituents of soil solutions. Their activities also vary nonlinearly with concentration, particularly at high concentrations. The activity coefficients of nonelectrolytes at low concentrations are approximated by

$$\log \gamma = -k_m I \quad (3.19)$$

where k_m is called the *salting coefficient* and I is ionic strength. Measured values of k_m range from 0.01 to 0.2 for common nonelectrolytes. The name salting coefficient comes from the tendency of nonelectrolytes to be less water soluble at increasing salt concentration, so that nonelectrolytes can be “salted out” of solution.

Like ions in aqueous solutions, the chemical activities of ions solids, and of water, also vary with concentration. Over the range of solute concentrations in soil solutions, however, the activity of water changes only negligibly from that of pure water. The chemical potentials of pure solids are defined as one, because any amount of the solid fixes the equilibrium activity of that substance in the aqueous solution. The activity of the aqueous solution is therefore independent of the amount of solid present.

The chemical potential of solid solutions, including impure minerals such as those in soils and rocks, is more difficult to define. Isomorphously substituted ions in a mineral change its activity and aqueous solubility from that of the pure mineral. Progress in defining solid activities has been slow. Soil minerals have often been assumed, by necessity, to be pure minerals and assumed to have activity = 1. This assumption is weak and is discussed later in this chapter.

3.3 COMPLEX IONS AND ION PAIRS

When ions and molecules interact closely, they lose their separate identities and are better thought of as complex ions or ion pairs. The $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ions are complex ions: The water molecules are closely attached to the central ion, with the group acting as one entity.

Complex ions are the combination of a central cation with one or more ligands. A *ligand* is any ion or molecule in the coordination sphere around the central ion, H_2O in the case of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. Water is usually taken for granted in complex ions and often disregarded. Ligands replace one or more of the water molecules in the primary hydration sphere. Ion pairs, on the other hand, are thought to form by ligand attachment in the second solvation sphere (Figure 3.3) and the bonding is weaker than in complex ions. Complex ions and ion pairs are synonymous with *inner-* and *outer-sphere complexes*. Many alkaline earth and transition metal cations are present in soil solutions as complex ions or ion pairs.

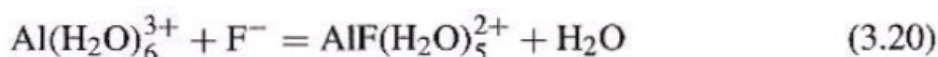


FIGURE 3.3. Diagram of an ion pair and a complex ion.

To associate with a central ion, ligands must compete with the water molecules in the central ion's solvation sphere and must lose some of the water molecules in their own solvation sphere. In addition, since many ligands are the anions of weak acids, H^+ competes with the central cation for the ligand. Forming a complex ion or ion pair involves competition between the cation and H^+ for the ligands, and between the water, OH^- , and ligands for the central cation.

The strength of association between the ions in solution is expressed by various equilibrium constants. *Stability (formation) constants* refer to complex ions and ion pairs; *hydrolysis (deprotonation) constants* refer to the loss of H^+ from the water ligands surrounding central cations. *Solubility products* refer to the aqueous ion activities in equilibrium with solid phases. Some "constants" are reported in the literature in terms of concentrations rather than activities. Such constants are misnamed, since they depend both on the concentration and on the nature of other ions in solution. Converting concentrations to activities gives a much more useful value.

The formation of complex ions is the result of cation–anion attractive forces winning out in the competition between cations and H^+ for the various ligands, including water. An example is the formation of the monofluoroaluminium complex ion



This reaction is exploited to extract reactive Al^{3+} from soils. Forming AlF^{2+} lowers the activity of $Al(H_2O)_6^{3+}$ in the water so the fluoride dissolves some Al^{3+} from the solid phase. The stability constant of this complex ion is

$$K_{AlF^{2+}} = \frac{AlF^{2+}}{(Al^{3+})(F^-)} \quad (3.21)$$

The waters of the hydration sphere are usually ignored in the equilibrium constant, because excess water is present in aqueous solutions, and the energy of the Al–F bond must be greater than that of the ion–water bonds for the complex to form. The concentration of the AlF^{2+} complex ion increases with increasing concentrations of Al^{3+} and F^- .

At the same time, H^+ competes for the fluoride ion. HF is a weak acid and its dissociation or acidity constant is

$$K_{HF} = \frac{(H^+)(F^-)}{HF} \quad (3.22)$$

Substituting Eq. 3.22 into Eq. 3.21 and rearranging yields

$$(\text{AlF}^{2+}) = K_{\text{AlF}^{2+}} K_{\text{HF}} \frac{(\text{Al}^{3+})(\text{HF})}{\text{H}^+} \quad (3.23)$$

The concentration of the AlF^{2+} complex ion increases with increasing HF and Al^{3+} concentrations and decreases with increasing acidity.

Increasing F^- concentrations encourage more F^- ligands to replace water ligands around Al^{3+} , to a limit of AlF_6^{3-} . The hexafluoroaluminium ion is, in fact, the complex ion removed during fluoride extraction of aluminium from soils, because of the high fluoride concentrations employed.

Ligands such as H_2O , OH^- , F^- , and CN^- occupy only one position around a central cation (Fig. 3.4) and are called *unidentate ligands*. Four of the six F^- ligands are in the plane of the Al^{3+} cation; the other two ligands are above and below the plane. *Bridging ligands* such as O^{2-} , CO_3^{2-} , and PO_4^{3-} can occupy one position in the coordination spheres of two different cations. This produces a *polynuclear complex* (nuclear referring to the central ion). The solubility of polynuclear complexes is usually less than mononuclear complex ions. Polynuclear complexes tend to polymerize further and precipitate from solution.

A *polydentate ligand* can occupy two or more positions around a cation and can surround the cation. Such ligands are usually large organic molecules called *chelates*, from the Greek word for claw. Some enzymes, for example, are polydentate ligands occupying several positions around a central cation while also bonding to substrate molecules. This results in a configuration that catalyzes chemical changes in the substrate. Soil organic matter strongly adsorbs Cu^{2+} , Zn^{2+} , Fe^{2+} , and other transition metal ions, probably by acting as a chelate.

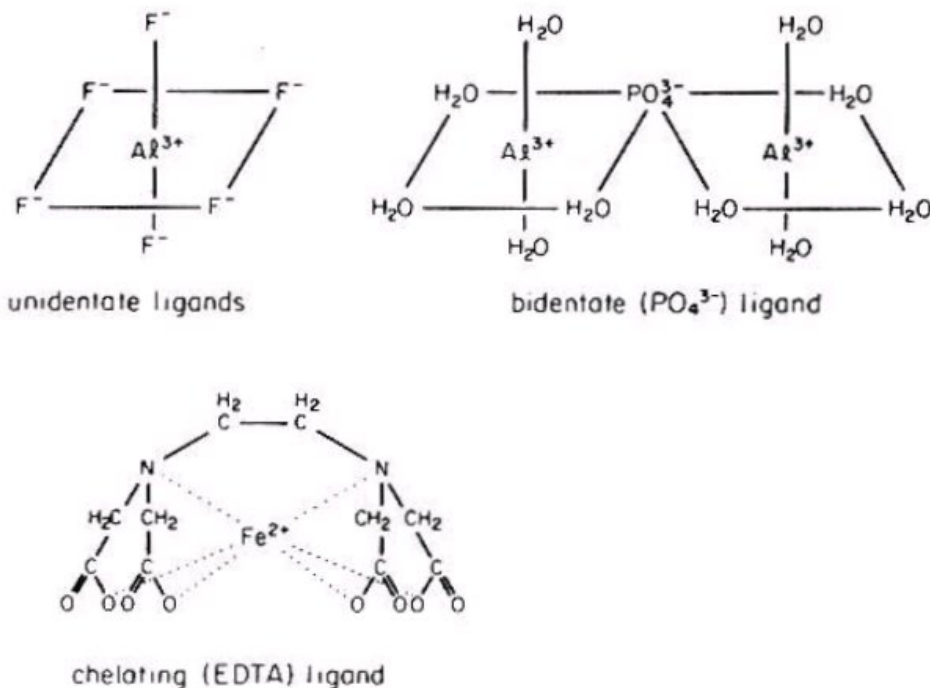
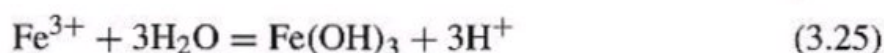


FIGURE 3.4. Schematic structure of the AlF_6^{3-} , binuclear Al-PO_4 , and EDTA-iron(II) complex ions.

An example of a chelating ligand is ethylenediaminetetraacetic acid (H_4EDTA) and its many relatives (Fig. 3.4). The six positions around Fe^{2+} are occupied by the two amine and four acetate groups. Chlorophyll and hemoglobin are also chelates. Chelates are quite soluble and tend to keep Fe, Zn, and Cu in solution for plant absorption. Chelates are also used to extract microelement and heavy metal ions from soils. The stability constant of the Fe(III)-EDTA complex is

$$K_{FeEDTA} = \frac{FeEDTA^-}{(Fe^{3+})(EDTA^{4-})} \quad (3.24)$$

The competing reaction for Fe(III) in soils is its dissolution/precipitation as $FeOOH$:

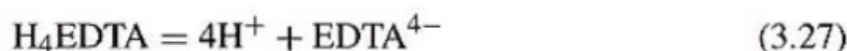


The solubility product of $Fe(OH)_3$ is

$$K_{sp} = (Fe^{3+})(OH^-)^3 = (Fe^{3+}) \left(\frac{K_w}{H^+} \right)^3 \quad (3.26)$$

where K_{sp} is the solubility product of $Fe(OH)_3$ and K_w is the dissociation constant of water, $K_w = (H^+)(OH^-) = 10^{-14}$.

H^+ competes by reacting/dissociating as H_4EDTA :



where the dissociation constant is

$$K_{H_4EDTA} = \frac{(H^+)^4(EDTA^{4-})}{H_4EDTA} \quad (3.28)$$

Substituting Eqs. 3.26 and 3.28 into 3.24 and rearranging gives the solubility of the Fe(III)-EDTA complex ion in equilibrium with $Fe(OH)_3$:

$$(FeEDTA) = K_{FeEDTA} K_{sp} K_{H_4EDTA} \frac{H_4EDTA}{K_w^3} \cdot H^+ \quad (3.29)$$

where K_w is the dissociation constant of water. Equation 3.29 can be further extended to include the reduction of Fe(III) to Fe(II). This reduction changes the solubility of hydrated iron and hence the stability of the EDTA complex.

The relations between EDTA and other chelates with cations in pure solution can often be applied to soil solutions by including suitable solid-phase controls and competition from other cations and hence related to ion uptake by plants. Lindsay and co-workers (1979) have carried out such calculations in detail.

At equal cation concentrations, transition metal cations compete more effectively for ligands than can alkali and alkaline earth cations. Transition metal ions have the advantage of being able to shift some electrons to better accommodate ligand configurations. The ability of unidentate ligands to shift electron orbitals and thus form stronger complex ions generally increases in the following order: $I^- < Br^- <$

Table 3.5. Stability constants of EDTA (ethylenediamine tetraacetic acid)^a

Metal Ion	log <i>K</i>
Li ⁺	2.8
Na ⁺	1.7
Mg ²⁺	9.0
Ca ²⁺	10.7
Ba ²⁺	7.8
Mn ²⁺	13.8
Fe ²⁺	14.0
Co ²⁺	16.0
Cu ²⁺	18.5
Zn ²⁺	16.3
Al ³⁺	16.1
Fe ³⁺	25.00
La ³⁺	15.4
Th ⁴⁺	23.2

(p*K*₁ = 2.0, p*K*₂ = 2.7, p*K*₃ = 6.2, p*K*₄ = 10.3)

^aFrom L. G. Sillen and A. E. Martell. 1974. *The Chemical Society Spec. Publ.* 25, London.

Cl⁻ < F⁻ < C₂H₅OH < H₂O < NH₃ < ethylenediamine < CN⁻. The strength of nitrogen-containing ligands is noteworthy in this list.

The relative ability of the transition metal ions to form complex ions is Mn²⁺ < Fe²⁺ < Co²⁺ < Ni²⁺ < Cu²⁺ > Zn²⁺ for the divalent cations and Cr³⁺ = Mn³⁺ > Fe³⁺ < Co³⁺ for the trivalent cations. The strongest complexing divalent cation is Cu(II). Fe(III) is the weakest complexing trivalent transition metal ion, but is stronger than other trivalent cations such as Al³⁺ and the lanthanides. The heats of hydration (Table 3.2), strengths of EDTA complexes (Table 3.5), and solubility products of metal hydroxyoxides (Table 3.3) also follow this general order, with water, EDTA, and OH⁻ as the respective ligands. Stability constants less than 10⁹ indicate the weaker ion-ion interaction of ion pairs.

Figure 3.5 shows how the distribution of EDTA complex ions changes with pH under representative soil solution conditions. The changes are due to competition between the cations for all of the ligands. The Fe-EDTA complex predominates in acid solutions, because of the great stability of Fe-EDTA complexes and weak competition from the low OH⁻ concentrations for Fe(III). The EDTA ligand prefers Fe(II and III) despite the high Ca²⁺ and Mg²⁺ concentrations in soil solution. Other transition metal ions are generally in low concentrations in soil solutions. In alkaline soils, however, the higher Ca²⁺ and Mg²⁺ concentrations and the very low solubility of Fe(III) hydroxide favor the formation of CaEDTA and Mg-EDTA complexes

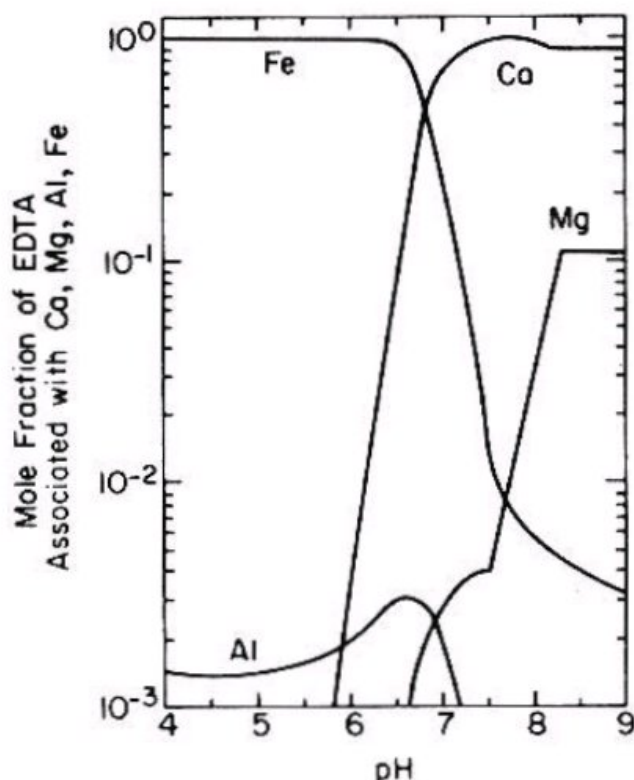


FIGURE 3.5. Mole fraction of EDTA in various complexes versus pH of hypothetical soil solutions. (From W. A. Norvell, 1974. In *Micronutrients in Agriculture* J. J. Mortvedt, P. M. Giordano, and W. A. Lindsay, (Eds.) Soil Science Society of America, Madison, WI.)

instead. This general picture holds true for many complexing ligands but shifts according to the values of the specific stability constants.

Another illustration of competition is during laboratory measurements of Ca^{2+} and Mg^{2+} in soil extracts. To ensure that all Ca^{2+} , Mg^{2+} , and EDTA, but only these ions, are present as complex ions, the solution is made alkaline to about pH 10 to precipitate transition metal ions. Then CN^- (which complexes strongly with the transition metals but weakly with Ca^{2+} or Mg^{2+}) is added to complex any remaining transition metal cations.

Ion pairs, or outer-sphere complexes, are written as CaSO_4^0 and CaCO_3^0 to distinguish them from their respective solids. The CaSO_4^0 and CaCO_3^0 ion pairs have been found to be particularly important in accounting for apparent supersaturation of CaCO_3 in groundwaters and drainage waters of arid regions. Magnesium also forms sulfate and carbonate ion pairs in many natural waters. Ion pair formation increases with increasing ion charge and concentration. Alkali metal ions such as Na^+ and K^+ form ion pairs only in highly saline soils and brines. Taking ion pair and complex ion formation into account has greatly increased our knowledge of the solid phases that govern ion concentrations in soil solutions.

3.4 HARD AND SOFT LEWIS ACIDS AND BASES

The reactions of water, H^+ , OH^- , and O^{2-} describe the aqueous solution behavior of many cations—alkali, alkaline earth, Al, and others. This is *Bronsted acid-base*

Table 3.6. Hard and soft Lewis acids and bases

Lewis Acids	Lewis Bases
HARD	
H ⁺ , Li ⁺ , Na ⁺ , K ⁺ Mg ²⁺ , Ca ²⁺ , Sr ²⁺ Al ³⁺ , Be ³⁺ , Si ⁴⁺ , Ti ³⁻⁴⁺ Mn ²⁺ , Fe ³⁺ , Co ³⁺ , Cr ³⁺	H ₂ O, OH ⁻ , O ²⁻ , CO ₃ ²⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ SiO ₄ ⁴⁻ , F ⁻ , NH ₃ aluminosilicates
INTERMEDIATE	
Fe ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ Zn ²⁺ , Pb ²⁺	NO ₂ ⁻ , SO ₃ ⁻ , Cl ⁻ , Br ⁻ , pyridine soil organic matter
SOFT	
Cd ²⁺ , Hg ¹⁻²⁺ , Cu ⁺ , Ag ⁺	S ²⁻ , CN ⁻

behavior. These cations also react strongly with oxygen-dominated ligands such as CO₃²⁻, SO₄²⁻, NO₃⁻, and silicates. These cations are the predominant exchangeable ions and the soluble and exchangeable anions in soil solutions.

The above cations and anions interact weakly, however, with another interesting ion group—Cu²⁺, Cd²⁺, Hg²⁺, S²⁻, CN⁻, and other organic groups—which tends to react within itself in preference to the oxygen-dominated group. Pearson called the oxygen-dominated group hard Lewis acids (cations) and bases (anions) and the second group, soft Lewis acids and bases (Table 3.6). Pearson suggested the general rule: “Hard Lewis acids tend to associate with hard Lewis bases; soft Lewis acids tend to associate with soft Lewis bases.”

Hard Lewis acids and bases have inflexible electron orbitals that form ionic bonds. The electron orbitals of soft Lewis acids and bases are more polarizable and more likely to form covalent bonds. Soft Lewis acids and bases are also called covalent-bonding ions and are “siderophile” (sulfur-loving) ions in the geology literature. Organic ligands and soil organic matter range from hard to soft Lewis bases.

This classification explains why, for example, Fe³⁺ reacts differently than Fe²⁺ in soils. Reduced oxidation states tend to be softer Lewis acids and bases. Hard and soft also explains why Cd²⁺ reacts quite differently than other cations of similar charge and size such as Ca, and why soil organic matter reacts with soft Lewis acids and also contributes greatly to the exchange capacity of hard Lewis acids.

3.5 SOIL REACTION COEFFICIENTS

Many of the hydroxyoxides listed in Table 3.4 exist in soils. Their ion activity products, as well as those of phosphates, carbonates, sulfides, and silicates, have been measured in soil solutions. Unfortunately, the ion activity products often differ widely from accepted solubility products in pure solutions, and also from soil to soil. The differences between ion activity products and solubility products is due

to nonequilibrium and the formation of solid solutions whose aqueous solubilities differ from the solubilities of pure compounds. The lack of equilibrium is due to slow diffusion of ions in the weathered surfaces of soil particles. As the ion diffuses into the denser, more crystalline and less weathered interior, its diffusion rate slows dramatically. Diffusion rates in the truly solid phase are essentially zero at room temperature. Diffusion is only significant where water enters into the solid and where weathering breaks up the crystal structure.

The ion activity products in soil solutions and tabulated solubility products should agree only if the solubility of a single phase dominates the system, if competing reactions are insignificant, if the single phase is reasonably pure, and if the system is close to equilibrium. This apparently holds true for gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and FeOOH . Measurements of the $(\text{Fe})(\text{OH})^3$ ion product in soil suspensions agree fairly well with the solubility product of amorphous FeOOH , $K_{\text{sp}} = 10^{-39}$. Apparently Fe(III) reacts rapidly and only with OH^- so that a single solid controls its solubility, including ion-exchange equilibria. Aluminium concentrations, on the other hand, appear to be controlled by slow processes, including weathering of aluminosilicates. The solubility product of gypsum probably holds because its solubility is great enough to swamp out any competing reaction.

Phosphate is associated with many phases of the soil, including organic matter. None of these phases predominates in all soils, and all have different dissociation strengths for phosphate. Hence, each should support a different phosphate concentration, and the strength of association decreases as the phosphate concentration increases for all of the phases. As a result, phosphate ions should distribute themselves among the various retention sites until, at equilibrium, all the ions have the same dissociation energy. The speed of these transformations may control soil phosphate concentrations rather than the equilibrium solubility of this distribution.

The rates of soil phosphate reactions also may differ from the rates of phosphate uptake by plants and of phosphate release by organic matter decay. This phosphate turnover would further upset soil phosphate equilibria. If a steady state (concentration is constant with time) existed between the soil and dissolved phosphate ions, it might be described by a reaction such as



where all of the many phosphate interactions with soil are combined into a single generalized reaction, so that

$$K_r = \frac{(\text{soil-H}_2\text{PO}_4)(\text{OH}^-)}{(\text{soil-OH})(\text{H}_2\text{PO}_4^-)} \quad (3.31)$$

where K_r is a reaction coefficient rather than an equilibrium constant. Equations 3.30 and 3.31 can be misleading. They have the form of equilibrium equations, but equilibrium does not exist. Also, the activities of soil-adsorbed ion such as soil-OH and $\text{soil-H}_2\text{PO}_4$ cannot be defined precisely. Equations like 3.30 describe an ongoing process rather than equilibrium.

3.6 MODELS OF THE SOIL SOLUTION

Strictly speaking, soils are always nonequilibrium systems. With care, however, a partial equilibrium or steady state can be attained by assuming that the soil solids do not change. This is the usual assumption in cation exchange and adsorption studies. Kittrick and co-workers were able to obtain near-equilibrium measurements of some soil minerals in studies requiring several years. From the resulting ion activities in solution, they were able to calculate some of the equilibrium constants used for the mineral stability diagrams shown later in this book.

Ion hydrolysis and solid dissolution reactions occur at the same time in the soil solution and many of these reactions are interdependent. One hydrolysis reaction that releases H^+ , for example, affects the other hydrolysis reactions and solids containing OH^- ligands. The advent of computers allowed rapid calculation of many simultaneous reactions, and this was soon applied to models that try to calculate the composition of the soil solution and natural waters.

The early models yielded approximate concentrations that reflected the understanding of the soil solution at the time. Later models have yielded better predictions of the soil solution's composition, but they are still only approximate. That reflects the complexity of the soil more than the inadequacy of modeling. The models predict ion interactions in the aqueous solution quite well. Reactions at the surface of colloidal particles are more complex, less understood, slower, and hence are more difficult to formulate. In addition, the models are forced to use the solubility products of pure, simple solids. Soil inorganic particles are far from pure compounds, are often poorly crystalline to amorphous, are not at internal equilibrium, and may not be in equilibrium with the aqueous phase. In addition, the reactions of soil organic matter are not known quantitatively; and soils are open systems, meaning that matter is continually being added and removed.

The models therefore reflect our level of knowledge of the soil solution and its interaction with soil solids. Since these models have the potential to predict the composition of natural waters (groundwater, lakes and streams, oceans as well as the soil solution), soil fertility, the effects of fertilizers and soil amendments, the effects of acid rain, and the attenuation and release of pollutants in soils, this important area of research should be actively pursued. The accuracy of the models, however, is still based on our understanding of the soil's chemistry and cannot be more accurate than that.

APPENDIX 3.1 THERMODYNAMICS

Chemical activity, heat of hydration, and equilibrium constant are parts of the very useful discipline called thermodynamics. Thermodynamics is the relation of matter and energy that predicts the direction and final result of chemical and physical reactions, but does not predict the rate or the path of reactions. This section introduces thermodynamic terms commonly encountered in the soils literature. Thermodynamic relationships are derived in detail in many physical chemistry texts.

Three disarmingly simple "laws" of thermodynamics that describe the relations of matter and energy have evolved into an elaborate structure that can obscure their initial simplicity. If an exception is found, the laws will be modified to include the exception. The laws have some background assumptions and require careful definitions. Chemical thermodynamics is dominated by the concept of *equilibrium*. Equilibrium is a state or condition that remains unchanged as long as energy and matter are neither gained nor lost from the system. An equilibrium system will return to equilibrium after a slight perturbation, such as a change in temperature or pressure.

Equilibrium principles require that a system be completely described by easily measured variables, such as temperature, pressure, and composition. These properties of the system define its *state*. The state is relatively easy to define for simple systems in the chemical laboratory, but is much more difficult to define in the complex systems of nature and soils. For example, the complete mineralogical composition of soils is difficult, if not impossible, to determine. The amounts and types of minerals in the clay fraction are known at best only semiquantitatively. In addition, the composition of each mineral can vary over a wide range and the weathered surfaces are different than the unweathered portion. Soil behavior also depends on the size, matrix, and interactions of soil particles. These are at present inadequately measured or defined. Wetting and drying can irreversibly change the arrangement of soil particles. Heating and drying can destroy organic compounds, change soil minerals, and markedly modify the composition of the soil solution.

Soils are nonequilibrium systems, but sometimes can be considered close enough to equilibrium to let equilibrium principles apply. The requirements are that (1) the rates of soil change are negligible in the time scale under consideration, (2) the perturbation does not change the composition of the solid phase, (3) the soil is homogeneous, and (4) the soil is a *closed system*—it does not gain or lose matter—during the experiment. None of these assumptions can be completely true, but the errors can be small if the experiments are done carefully.

The "laws" of thermodynamics describe physical and chemical behavior to which we have not yet found exception. Claimed exceptions to the laws of thermodynamics have thus far proved to be unrecognized, and often very subtle, violations of the conventions of thermodynamics. The first law—matter and energy are conserved (neither created nor destroyed) during a process—is an idea that already appealed to medieval philosophers. During the late 1700s and early 1800s, careful measurements of water pumps and steam engines showed, however, that although mass was conserved, some energy was always lost. Furthermore, the faster the pumps and engines ran, the greater the loss of this energy; that is, the process was less efficient at greater speeds.

Rather than discard the first law despite this apparent flaw, people changed the definitions, and introduced the second law, so the first law would still be true. The first law now deals with total energy, which is conserved.

If a reaction proceeded infinitely slowly, the first law would still hold true. Real-world reactions, however, proceed at a finite pace. The second law takes this into account by stating that some energy, called *entropy* S , is irretrievably lost during any process. This brings thermodynamics much closer to the real world. The available

energy (*Gibbs free energy* G) obtained from a process is always less than the energy input H (*enthalpy*) or first law energy

$$\Delta G = \Delta H - T \Delta S \quad (3.32)$$

where T is the absolute temperature and the Δ refers to a difference between two values. We do not know the absolute energies; we can only measure the difference in energy between two states. The terms in Eq. 3.32 are given positive or negative signs according to the change within the *system*. The system might be a volume of soil or a flask containing a soil suspension, considered as separate from its surroundings. If the system loses energy such as heat or work to the surroundings, the sign is negative because the system has less energy than before. If the system gains energy from the surroundings, the sign of the energy terms is positive.

Entropy is defined so that it is positive and increasing during spontaneous reactions, reactions that proceed without energy input. Entropy is the energy lost during the reaction. This energy ultimately is radiated into space and is made up for by solar energy plus some energy from the earth's interior. Without solar and earth energy to compensate for the continual loss of entropy, the earth would eventually reach equilibrium and life would end. Some people consider entropy to be the unavailable energy or a bookkeeping entry that corrects the first law. Others prefer to describe entropy in more physical terms, as the friction in all processes, or as the energy lost in rearranging ions and molecules during chemical reactions. Increasing entropy implies increasing randomness or disorder of matter; decreasing entropy implies structural ordering.

Soon a loophole was discovered in the second law. When the temperature is absolute zero, the second law reduces to the first law and becomes unnecessary. So the third law—that we cannot reach absolute zero—was invoked to keep the second law universally valid. Corollaries of the laws are that entropy strives toward a maximum, free energy strives toward a minimum, and when the free energy is at a minimum, the system is at equilibrium.

Systems far from equilibrium, such as living systems that are negative entropy because they are so ordered, may be better described by *irreversible thermodynamics*. Living systems are greatly ordered and generally have active energy flows; examples are ecological systems having organisms with elaborate organic compounds closely interacting with other compounds, active population growth, and photosynthesis. Irreversible thermodynamics attempts to describe this energy flow. Irreversible thermodynamics has found little application in soil chemistry. In many cases, soil minerals and solutions are close enough to equilibrium that equilibrium and reversible thermodynamics suffice. Often a soil process in the laboratory or field is viewed as reacting much more rapidly than the overall soil. Then the process can be treated essentially as if it were an equilibrium process.

The three laws of thermodynamics and Newton's laws of physics govern the behavior of matter and energy in the systems that we normally deal with. The 20th-century developments of quantum and statistical mechanics deal with atomic and subatomic behavior. One test of their validity is that they yield the laws of thermo-

dynamics when expanded to larger systems. So far, soil behavior has not required quantum or statistical mechanics for explanation.

Soils are sensitive to changes brought about by drying, wetting, leaching with monovalent salt solutions, acidification and basification, changing ionic strength, changing oxidizing-reducing conditions, and changing the soil-solution ratio. The bulk of the soil is quite resistant to change, but soil surfaces are vulnerable. Some of these reactions revert back slowly if at all to the previous state. This irreversibility weakens assumptions of equilibrium. Experiments that hope to utilize equilibrium principles should not inadvertently change the chemistry of the soil's surface.

A3.1.1 Gibbs Free Energy

The thermodynamic term of widest use in soil chemistry is the *free energy*, or more explicitly, the *Gibbs free energy*. This is the energy of a substance or a reaction that, at constant temperature and pressure, is available for subsequent use. Energy drives chemical reactions and ΔG is the most widely useful. It is directly related to (1) the activity or chemical potential, (2) the energy of formation of compounds, (3) the equilibrium constant of a reaction, and (4) the electrode potential. The first three are discussed here; the electrode potential is discussed in Chapter 4.

The ΔG can be defined as

$$\Delta G = V \Delta P + S \Delta T + f(\text{compositional, electrical, gravitational potentials}) \quad (3.33)$$

where V is the volume, ΔP the pressure change, and ΔT the temperature change. At constant temperature and pressure

$$\Delta G_{T,P} = f(\text{compositional, electrical, gravitational potentials}) \quad (3.34)$$

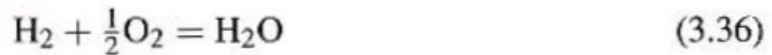
The Gibbs free energy is determined by changes in composition, gravity, and electrical potentials. Chemistry is usually concerned only with variations in composition potentials. The gravitational potential arises from differences in elevation, such as the "water head" or hydraulic potential of soil physics, but can usually be ignored by soil chemists. Electrical potential is an important consideration near charged surfaces such as soil particles. When dealing with an aqueous solution, however, the Gibbs free energy at constant temperature and pressure is determined solely by the composition and concentration of the solution.

The most useful concentration unit for solutions is the chemical activity a (Section 3.2). The change in free energy with the amount of solute is

$$\Delta G = RT \ln a = 5.71 \log a \quad (3.35)$$

where the units of ΔG are kJ mol^{-1} . The free energy decreases as the solute becomes more dilute. The change is calculated from an arbitrary standard state of solute, usually defined as an ideal 1 M solution, where $a = 1$. At solute activities up to unity, the activity of the solvent (water) is usually assumed to be unity, that is, to be unaffected by solute concentration.

The ΔG value of a certain state is the difference in free energy between that state and a *standard state*. For the free energy possessed by a chemical compound, the usual standard state is its free energy at 25° C (298.15 K) and 10^5 Pa (1 atm) pressure. The elements are assigned free energies of zero. The energy of formation is absorbed or released by compounds when they form from their elements. For example, careful measurement of the reaction

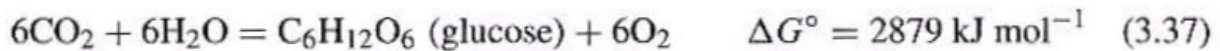


at standard conditions (298.15 K and 10^5 Pa) yields 237 kJ of available energy per mole of water formed. Thus, $\Delta G^\circ = -237 \text{ kJ mol}^{-1}$ with the superscript denoting standard conditions. This reaction releases energy to its surroundings, so the sign of ΔG° is negative, indicating that the system has less energy than before.

Reactions that release energy and leave the system in a lower energy state, a more stable state, than before are *spontaneous*. The second law states that systems will strive to reach the lowest energy level. Thermodynamics says only that a reaction will proceed and not what the reaction rate will be. The hydrogen and oxygen in reaction 3.36 can coexist for centuries without reacting until a catalyst or spark is introduced.

The free energies of formation of many compounds and ions have been measured and compiled. Table 3.7 contains values for the ΔG° of formation of some compounds relevant to soil chemistry.

The change of free energy during a reaction is the difference between the free energies of the products and those of the reactants. An important energy reaction in nature is photosynthesis, the formation of glucose:



The sign of the free energy change of this reaction is positive, because solar energy has come from the surroundings and been trapped in the glucose molecule. The free energy of the reaction is the difference between the free energies of formation of the products (glucose and oxygen) and of the reactants (carbon dioxide and water):

$$\Delta G_{3.37} = \Delta G_{\text{glucose}} + 6(\Delta G_{\text{O}_2}) - 6(\Delta G_{\text{CO}_2} + \Delta G_{\text{H}_2\text{O}}) \quad (3.38)$$

Each term is the value per mole so it is multiplied by the appropriate coefficient from Eq. 3.37. Rearrangement yields

$$\Delta G_{\text{glucose}} = \Delta G_{3.37} - 6(\Delta G_{\text{O}_2}) + 6(\Delta G_{\text{CO}_2} + \Delta G_{\text{H}_2\text{O}}) \quad (3.39)$$

The ΔG of formation of oxygen is assigned a value of zero, because it is a pure element. The ΔG of formation of carbon dioxide ($-394.3 \text{ kJ mol}^{-1}$) and other compounds is available from many handbooks. The ΔG of formation of glucose is thus

$$\Delta G_{\text{glucose}} = +2879 - 0 + 6(-394.3) + 6(-237.2) = -910.4 \text{ kJ mol}^{-1} \quad (3.40)$$

Table 3.7. Standard Gibbs free energies of selected compounds at 25° C (*a* is activity and *P* is partial pressure or mole fraction of gas)

Formula	Name or State	ΔG° (kJ mol ⁻¹)	Source
Al(OH) ₃	Gibbsite	-1 151	3
Al ₂ Si ₂ O ₅ (OH) ₄	Kaolinite	-3 783	3
M _{0.56} (Al _{3.03} Mg _{0.58} Fe _{0.45} (Si _{7.87} Al _{0.13})O ₂₀ (OH) ₄)	Montmorillonite	-10 330	4
CaCO ₃	Calcite	-1 129	1
CaSO ₄ · 2H ₂ O	Gypsum	-1 797	1
Fe ₂ O ₃	Hematite	-741	2
Fe(OH) ₃	(Crystalline?)	-694.5	2
FeCO ₃	Siderite	-674.0	2
FeS ₂	Pyrite	-150.6	2
MgCO ₃	Magnesite	-1 029	2
MnO ₂	Pyrolusite	-464.8	2
MnCO ₃	Rhodochrosite	-817.6	2
MnS	Alabandite	-233	2
HNO ₃ and NO ₃ ⁻	<i>a</i> = 1	-110.6	1
NH ₃	<i>P</i> = 1	-16.64	1
NH ₄ OH	<i>a</i> = 1	-263.8	1
H ⁺	<i>a</i> = 1	0.0	1
OH ⁻	<i>a</i> = 1	-157.1	2
H ₂ O	<i>a</i> = 1	-237.2	1
H ₃ PO ₄	<i>a</i> = 1	-1 143	1
PO ₄ ³⁻	<i>a</i> = 1	-1 019	1
K ⁺	<i>a</i> = 1	-282.0	2
KAlSi ₃ O ₈	Feldspar	-3 581	2
KAl ₃ Si ₃ O ₁₀ (OH) ₂	Muscovite	-5 558	3
SiO ₂	Quartz	-8 567	1
Si(OH) ₄	Soluble silica, <i>a</i> = 1	-1 317	1
SO ₂	<i>P</i> = 1	-300.2	1
H ₂ S	<i>P</i> = 1	-33.6	1
H ₂ SO ₄ and SO ₄ ²⁻	<i>a</i> = 1	-744.6	1
TiO ₂	Rutile	-888.2	2
CO ₂	<i>P</i> = 1	-394.3	1
CH ₄	<i>P</i> = 1	-50.75	1
H ₂ CO ₃	<i>a</i> = 1	-623.2	1

1. From D. D. Wagman et al. 1968. Selected values of chemical thermodynamic properties. *U.S. Bur. Standards Tech. Notes 270-3 and -6*, Washington, DC.

2. From R. M. Garrels. 1960. *Mineral Equilibria*. Harper, New York.

3. From S. V. Mattigod. 1976. Ph.D. Dissertation, Washington State University, Pullman.

4. J. A. Kittrick. 1971. *Soil Sci. Soc. Am. Proc.* **35**:140.

When reaction 3.37 reverses during respiration, 1 mol of glucose liberates -2879 kJ of available energy to fuel the life processes of living organisms.

A third important facet of the Gibbs free energy is its relation to the equilibrium constant of a reaction. A reaction proceeds until the components are at their lowest energy level, the most stable state. This state is defined by the equilibrium constant K :

$$\Delta G = RT \ln K = 5.71 \log K \quad (3.41)$$

Equation 3.41 requires that the standard states of the products and reactants be known, that the components can be defined quantitatively and in a thermodynamic sense. In soils and much of nature these definitions are rarely possible. The states of ions or molecules in soil systems, and in probably all colloidal systems, are ill-defined thermodynamically. In rigorous thermodynamic terms even ions are undefined. Soil reactions, because of the nonequilibrium in soils and the lack of defined standard states, yield reaction coefficients, rather than reaction constants, and their values vary with soil conditions.

APPENDIX 3.2 SOLID SOLUTIONS AND OPEN SYSTEMS

The thermodynamics of solid mixtures and solid solutions would seem to hold great promise for soil chemistry, as much as the thermodynamics of aqueous solutions has proved useful, but it has been largely neglected. The neglect of solid solutions is partly due to an incompatibility between classical thermodynamics and nature. Nature and soils are more complex and they are *open systems*—energy and matter flow in and out of the system being studied. Nonetheless, some of the principles of solid mixtures are tacitly applied to ion exchange equations and adsorption studies. Direct applications of the thermodynamics of mixtures to soils may have considerable merit. The necessary assumptions are similar to those that have already been accepted in adsorption and cation exchange studies.

Strictly speaking, thermodynamics applies only to total equilibrium and to *closed systems*. A closed system gains and loses no matter during the reaction. Soils steadily lose matter during weathering and gain matter by aerial deposition, rain, and tectonic movements. Soils also are not at total equilibrium; the world would be sterile if nature were at total equilibrium.

Soil chemistry cannot afford the luxury of rigorous thermodynamics and instead has to stretch and bend the rules into what is called extrathermodynamics, but the bending and stretching must be done wisely. Cation exchange, solubility, Donnan, and adsorption studies find use in soils and assume equilibrium and a closed system during the experiment. Applying the thermodynamics of solid solutions to the reaction between the soil solution and soil particles requires the same rule bending as the other studies.

When substances in liquids or solids mix completely on an atomic scale, that is, when they mix homogeneously and randomly, the mixing usually decreases the es-

caping tendency of the components. The escape can be in the form of molecules evaporating from a liquid mixture, or of Ca and Mg ions dissolving into water from dolomite $\text{CaMg}(\text{CO}_3)_2$. Other examples of escaping tendency are cations exchanging from the mixture of cations on soil surfaces, phosphate desorbing from soil solids, and trace ions dissolving from silicate minerals.

Ions in solids cannot mix as randomly as can the components of gases and liquids. Mixing in glasses is close to random; ions in crystals are mixed but confined to fixed positions. This degree of mixing in crystals is sufficient to allow the thermodynamics of mixing to apply, and the mixing greatly affects the aqueous solubility of the ions in these solids. The general name of these solid mixtures is *solid solutions*; Hildebrand named crystalline solid solutions with their more limited mixing as *regular solutions*; the mixing of ions in solids is regular and repeated.

One example of the effect of mixing on the free energy or escaping tendency is the evaporation of a mixture of two organic liquids. When hexane is mixed with heptane, hexane's escaping tendency decreases. The escaping tendency is measured by its partial pressure P , which depends on hexane's volatility in the pure state and its concentration in the mixture, its degree of mixing:

$$P_{\text{hexane}} = g P_0 C_{\text{hexane}} \quad (3.42)$$

where P_0 is the vapor pressure of pure hexane, C is its mole fraction concentration in the mixture, and g is the activity coefficient that accounts for deviation from ideal mixing. Mixing increases the randomness of the hexane molecules, increases hexane's entropy, and therefore decreases its free energy, escaping tendency, and vapor pressure. Alternatively, the probability of a hexane molecule evaporating from a mixture is less than if evaporating from pure hexane, because fewer hexane molecules are at the surface.

Similarly, the escaping tendency, or aqueous solubility, of an ion depends on its bonding strength to the other ions of the solid. For ions on the surface, the escaping tendency depends on the extent of its mixing on the surface. As an example of the effect of solid mixing, the aqueous solubility of AlPO_4 is expressed by AlPO_4 's solubility product when the mineral is pure:

$$K_{\text{sp}} = \frac{(\text{Al})(\text{PO}_4)}{a_{\text{AlPO}_4}} \quad (3.43)$$

For pure AlPO_4 , the activity $a = 1$. When the phosphate ions are instead adsorbed on the surface of $\text{Al}(\text{OH})_3$, the phosphate ions behave as if they are AlPO_4 mixed with $\text{Al}(\text{OH})_3$. The solubility of AlPO_4 expressed by its *ion activity product* $(\text{Al})(\text{PO}_4)$ in the aqueous phase will be less than its solubility product because mixing increases the entropy of AlPO_4 in the solid phase and reduces its aqueous solubility. Its solubility in the mixture on the surface is

$$\text{IAP}_{\text{AlPO}_4} = g K_{\text{sp}} C_{\text{AlPO}_4} \quad (3.44)$$

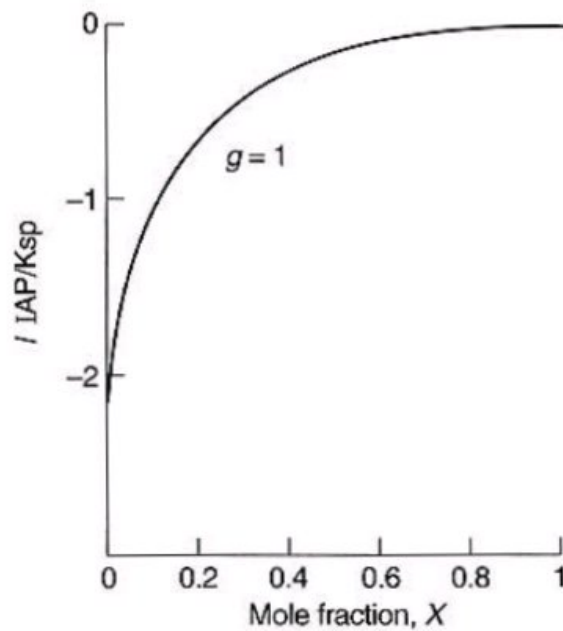


FIGURE 3.6. Change of relative equilibrium aqueous solubility, IAP/K_{sp} , of a component in a solid solution as a function of its composition in the solid. The solid solution is assumed to be ideal. (From H. L. Bohn, 1992. *Soil Sci.* 154:357.)

where g is the activity coefficient, K_{sp} is the solubility product of pure $AlPO_4$, and C is the mole fraction of phosphate on the $Al(OH)_3$ surface.

Figure 3.6 shows the effect of this solid solution mixing on the aqueous solubility of a substance assuming ideal mixing, $g = 1$. Mixing has little effect on the IAP/K_{sp} ratio of a substance until its mole fraction is <0.5 . The reduced aqueous solubility due to this mixing should be pronounced for trace ions in the soil solution such as phosphate and the trace metals, but insignificant for Si, Al, and Fe.

The activity coefficient g is an index of the deviation from ideal mixing. In ideal mixing, only the mixing entropy affects the escaping tendency. Mixing in nature is nonideal; molecular and ionic interactions change the amount of interaction and therefore affect the activity coefficient. The activity coefficients of solutes in water are generally <1 because ions interact with each other so their effective concentration is less than their actual concentration. Activity coefficients of solid components are usually >1 because substituted ions usually do not fit easily into the solid's structure. The structural stresses imposed by substitution tend to expel the ions into the aqueous solution. This somewhat counteracts the decreased aqueous solubility caused by the entropy of mixing and yields activity coefficients >1 . Each ion is different and fits differently into soil mineral structures. The usual result is that the ion's solubility is greater than if it mixed easily into the structure, hence $g > 1$, but not enough to overcome the effects of the mixing entropy. Early measurements indicate that the g values for ions like Al that are common in soil minerals, and presumably substitute easily, are about $g = 3$ to 5. For ions like phosphate and Ca that do not substitute easily into aluminosilicates, $g \geq 20$.

Like activity coefficients in aqueous solutions, solid activity coefficients are concentration dependent. As more phosphate ions mix on the surface of $Al(OH)_3$, for example, the hydroxide structure becomes more and more strained. The strain is re-

flected in a positive deviation from ideal mixing. PO_4 ions mix less easily because other PO_4 ions are already on the surface, and the activity coefficient increases in value. The $\text{Al}(\text{OH})_3$ tries to release the strain by trying to expel phosphate from the surface. As more phosphate is added, AlPO_4 eventually becomes more stable than the mixture and AlPO_4 precipitates as a separate phase.

Solid activities have been ignored largely because of a misunderstanding in our early chemistry training. The solubility product of Al hydroxide in chemistry texts, for example, is written as

$$K_{\text{sp}} = (\text{Al})(\text{OH})_3 \quad (3.45)$$

Equation 3.45 is accurate only in a pure system that contains only Al and OH ions and water. In that system the activity of Al hydroxide is one. For systems containing other components, such as aluminosilicates and Al substituted into FeOOH , a more complete expression of Al solubility is

$$K_{\text{sp}} = \frac{(\text{Al})(\text{OH})_3}{\text{Al}(\text{OH})_{3, \text{solid}}} \quad (3.46)$$

and

$$\text{IAP}_{\text{Al}(\text{OH})_3} = g K_{\text{sp}} C_{\text{Al}(\text{OH})_3} \quad (3.47)$$

The aqueous solubility of Al can be related to the solubility of $\text{Al}(\text{OH})_3$ even though that mineral may not be present. The solid activity of $\text{Al}(\text{OH})_3$ is gC . The aqueous solubility of Al depends on the equivalent concentration of $\text{Al}(\text{OH})_3$ in the solid phase. The activity of the solid is defined by the activity of the ions in the aqueous solution. The IAP is a measurable property of the system, so the solid activity is a thermodynamic property.

The concentration of Al hydroxide in soils is usually high enough that Eq. 3.45 is adequate and Eq. 3.46 is unnecessary. That is probably not true for ions in trace concentrations in soils. The mole fraction concentrations of phosphate and transition metal ions in soils are $\ll 0.01$. So soil phosphate solubility at "equilibrium" can be orders of magnitude less than the solubility of pure Al phosphate, as many soil measurements show. We can call it equilibrium because the solubility changes slowly to imperceptibly with time. If anything, the aqueous phosphate concentration decreases with time as the surface Al ions slowly diffuse into the weathered surface, mix further with other ions, and further increase their entropy. Simple AlPO_4 solubility product equivalent to Eq. 3.45, on the other hand, predicts that the phosphate concentration will increase with time.

Mixing on soil surfaces explains some soil phenomena very well. Mixing explains why soils can adsorb virtually every ion from soil solutions and can retain those ions much more tightly than can the ion's own hydroxyoxides, or retain phosphate more tightly than Al phosphate. This happens even though soil minerals are continuously losing their own components by weathering. Soil "adsorption sites" are areas where ions from the soil solution can mix with ions on soil surfaces. The mixing ability

varies with the kind of ions on the soil's surfaces and with the ability of the aqueous ion to bond strongly with those surface ions.

Soil is an open system. Weathering carries away substances from the soil; wind and rain add others. The surfaces of soil particles reflect these processes as well as the composition of the internal part of the particles. Because the particle and its surface do not have the same composition, the particle is not at equilibrium with itself. Ion diffusion within crystals is slow enough that this disequilibrium can be ignored.

In the weathered surfaces of soil particles where some semiliquid water may be present, ion diffusion may be fast enough to affect laboratory and field experiments. The slow removal of phosphate ions by soils from the aqueous phase may be due to the slow diffusion of PO_4 to Al and Fe ions within the weathered surface. The increasing strength of trace metal retention by soils with time may similarly be due to such diffusion into the semisolid, weathered surfaces of soil particles.

Ion activities in the soil solution can also be treated as being governed by the *saturation index* of a mineral:

$$\text{Saturation Index} = \frac{\text{IAP}}{K_{sp}} \quad (3.48)$$

From Eqs. 3.47 and 3.48, the saturation index equals the mineral's solid activity coefficient times its mole fraction in the solid phase:

$$\text{Saturation Index}_i = g_i C_i \quad (3.49)$$

APPENDIX 3.3 KINETICS

Thermodynamics predicts that substances will react until they reach their most stable states, but does not say how the most stable state will be achieved or how long it will take. Not all reactions lead immediately to the most stable states, and some reactions are exceedingly slow. Kinetics is the study of these reaction *mechanisms*: the rates, paths, and intermediate products of chemical reactions.

A substance put in conditions in which it is unstable will sometimes not react at all. A mechanical example of such "metastable equilibrium" is a rectangular block standing on end. It will not reach the more stable state of lying on its side until it is pushed and lifted so that its center of gravity is beyond its edge.

In chemical reactions, pushing and lifting the block correspond to activation energy. A mixture of H_2 and O_2 gases will not react until a spark or high temperature provides sufficient activation energy to greatly perturb the metastable equilibrium and allow the gases to react. Figure 3.7 shows the change in energy of a mixture of substances A and B that requires some activation energy to create the activated state AB^* before it degrades to C and D. Photosynthesis is an example of this process. Sunlight provides the activation energy that creates an activated state, glucose, which is metastable. The activated state returns to the stable initial states, CO_2 and H_2O , through a path of metabolism and decay that is as intricate as photosynthesis.

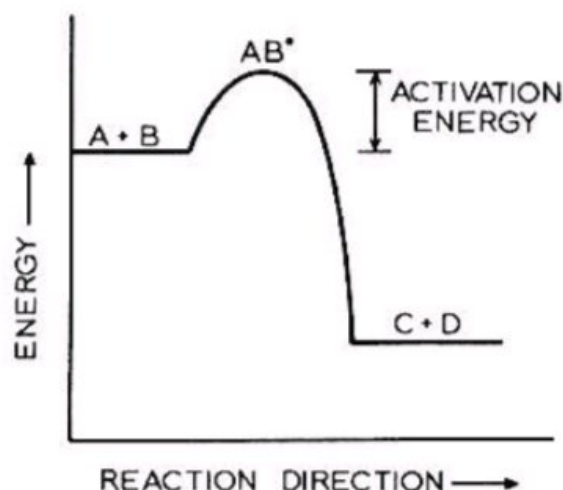


FIGURE 3.7. A representation of the extra energy (activation energy) needed to carry out the reaction $A + B \rightarrow C + D$. AB^* is the intermediate, activated complex.

Nitrogen fixation, denitrification, soil weathering, phosphate fixation, clay mineral degradation, and potassium and transition metal fixation are problems for which the reaction rates are usually as, or more, important than equilibrium. Most soil chemical applications of kinetics have been in soil microbiology and soil biochemistry, where the lack of equilibrium is more obvious. The use of kinetics in inorganic soil chemistry will undoubtedly broaden in the future. It can even be argued that kinetics is basic to thermodynamics, because equilibrium is the condition where opposing reaction rates are equal.

Small amounts of some substances can increase reaction rates enormously. These substances, when left unchanged by the reaction, are called *catalysts*. Perhaps the simplest type of catalytic action occurs when a surface adsorbs the reactants so that they remain in close proximity for relatively long periods of time. The probability of forming a new compound from the reactants then is much greater than if they merely collide and rebound in a gaseous or liquid phase. Soil surfaces may act as catalysts in this way.

Catalysts lower the activation energy barriers that hinder reactions. The activation energy requirement can arise from many chemical and physical factors, and the mechanisms by which catalysts lower the activation energy are probably just as numerous. Iron, manganese, and other transition-metal ions catalyze electron transfers during oxidation–reduction reactions. Enzymes are the organic catalysts indispensable for most reactions of living organisms.

Reaction inhibitors slow reaction rates. Nitrogen mineralization and nitrification (conversion of organic nitrogen and ammonium to nitrate) rates in soils, for example, can be slowed temporarily by chemicals that specifically slow or stop the microorganisms involved. Toxic metals can also operate as enzyme inhibitors, by replacing the metal coenzyme portion of an enzyme and thereby inactivating it.

Kinetics is being employed increasingly to study the soil chemistry of carbon, nitrogen, potassium, phosphate, and trace metals. The soil reactions of these elements are often slow enough to be experimentally measurable. Because carbon and nitrogen cycle back and forth between soil, water, plants, animals, and atmosphere faster than

the rates at which they reach their most stable thermodynamic states, kinetics is an appropriate tool with which to investigate their behavior.

For inorganic ions, the reactions themselves can be very fast, but the ions may have to diffuse through soil pores before they reach a reaction site. The ions may also have to diffuse through the weathered surface. Diffusion processes lend themselves to kinetic treatment. With multiple diffusion and reaction processes going on simultaneously, the kinetic treatment can become very complex.

A3.3.1 Reaction Order and Rate Constants

One approach of kinetics is to describe the dependence of reaction rates on reactant concentrations. For instance, the rate of phosphate fixation depends at least partly on the amount of fertilizer added, and the rate of denitrification (the conversion of soil nitrogen, usually nitrate to N_2 and N_2O) depends on soil solution nitrate concentrations. Kinetics relates reaction rates and reactant concentrations by means of the reaction order and the reaction rate constant. The denitrification rate ($-\Delta NO_3^- / \Delta t$) is presumably related to soil nitrate concentration by

$$-\frac{\Delta NO_3^-}{\Delta t} = k \Delta \{N_2O\}^n = k' \{\text{soil } NO_3^-\}^n \quad (3.50)$$

where k and k' are the reaction rate constants or coefficients, n is the reaction order, and braces denote concentrations. The negative sign indicates that nitrate is disappearing, and the positive sign indicates the production of N_2 and N_2O gases.

In pure systems under carefully controlled conditions, the reaction order is often 0, 1, or 2. These reaction rates can be plotted linearly with respect to time by choosing the appropriate concentration axis (Fig. 3.8). The reaction order can be obtained by fitting data to such plots. Zero-order reaction rates are independent of the amount or concentration of the reactant studied:

$$-\frac{\Delta C}{\Delta t} = k \quad (3.51)$$

where C is the concentration of some substance that is disappearing at a rate that is constant with time.

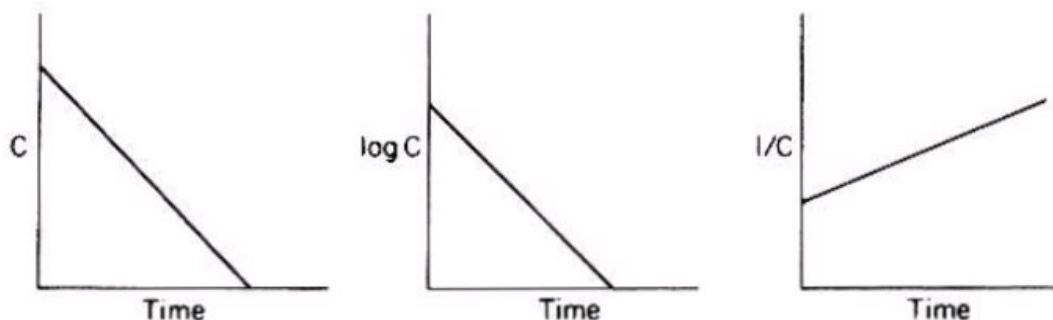


FIGURE 3.8. Zero-, first-, and second-order reactions plotted linearly with time. Note the varying units of the vertical axis.

The most common order found is first order, in which the reaction rate depends on the concentration of one reactant A:

$$-\frac{\Delta[A]}{\Delta t} = k[A][B] \quad (3.52)$$

This order can be obtained by "swamping" the system with the other components so that reactant A is rate limiting.

Second-order reactions depend on the concentrations of two reactants, or on the concentration of one reactant squared. The reaction of A and B to form D, for example, might follow the equation

$$\frac{\Delta D}{\Delta t} = k[A][B] \quad (3.53)$$

The sign of the left side is positive because D is increasing. If the concentration of B were much higher than that of A, the reaction rate would appear to depend solely on A. The reaction rate would be pseudo-first-order with respect to A and almost pseudo-zero-order with respect to B. The order of a reaction therefore depends on the conditions of the experiment.

The rates of soil adsorption reactions may also depend on the exponential of the amount already adsorbed. Phosphate adsorption by soils, for example, sometimes follows the Elovich equation:

$$\frac{\Delta A_{\text{ads}}}{\Delta t} = \alpha e^{-\beta A_{\text{ads}}} \quad (3.54)$$

where A_{ads} is the amount already adsorbed and α and β are empirical constants. Because of its two constants, this equation is more easily fitted to experimental data. The equation is plotted in Fig. 3.9, where α is the slope of the line. Reaction mecha-

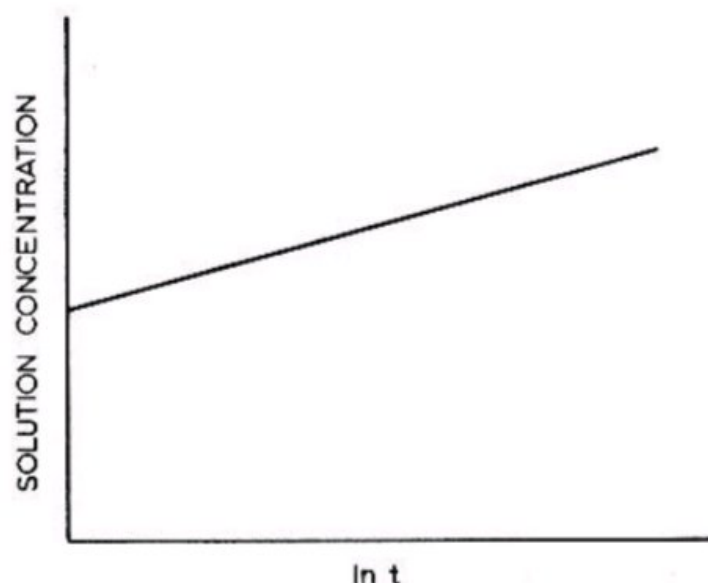


FIGURE 3.9. Plot of the Elovich adsorption equation 3.54.

nisms sometimes can be inferred from measured reaction orders. After ensuring that no other reactions are rate limiting, the reaction mechanisms are inferred by splitting the reaction into hypothetical step reactions until the sum of the orders equals the measured order. Insuring that the reaction in question limits the reaction rate is difficult for soils. The number of steps between reactant and product can be very large.

Reaction rates in soils are more complex than those in pure systems. Secondary and side reactions are difficult, if not impossible, to control. The measured reaction order is therefore usually fractional rather than a whole number because other reactions are usually going on at rates different from the one in question. If only the total change of a component is measurable, the overall reaction rate and order are weighted according to the relative contribution of each reaction.

In the denitrification example (Eq. 3.50), the rate of nitrate loss depends also on microbial activity and therefore on the presence of an energy source:

$$-\frac{\Delta[\text{NO}_3^-]}{\Delta t} = k[\text{soil NO}_3^-]^n [\text{available C}]^m \quad (3.55)$$

The reaction order is the sum of n plus m . Competing reactions of different rates, and reverse reactions, are the rule in nature rather than the exception. Reaction orders of such complex systems are usually nonintegral. Laboratory or field measurements are often possible only if all variables except the one of interest are held constant. Because the effects of only one or a few variables are measured, the reaction rate is incompletely described and the order is actually a pseudo-order. The term "pseudo" unfortunately has a disparaging connotation. Here it implies only that the system is too complicated to measure completely.

Determining the rate constant and order of a reaction is tedious and time-consuming. For many studies, this detail is unwarranted and the *half-life* is measured instead. The half-life is the time required for half of the original concentration of reactant to disappear. For the particular case of a first-order reaction, the half-life ($t_{1/2}$) is directly related to the reaction rate constant k by

$$t_{1/2} = \frac{\ln C_0/2}{k} = \frac{0.693}{k} \quad (3.56)$$

where C_0 is the original reactant concentration. Because many soil studies are carried out under conditions involving only one experimental variable, the pseudo-orders of the reactions may be close to unity. In these cases the half-life is a useful semiquantitative indicator of reaction rate.

A3.3.2 Temperature Effects

Higher temperatures increase the energy and probability of particle collisions. These, in turn, generally increase reaction rates. Measuring reaction rates at various temperatures can provide useful clues about reaction mechanisms. Figure 3.10 shows the effect of temperature on the rates of three types of reactions. The exponential rise

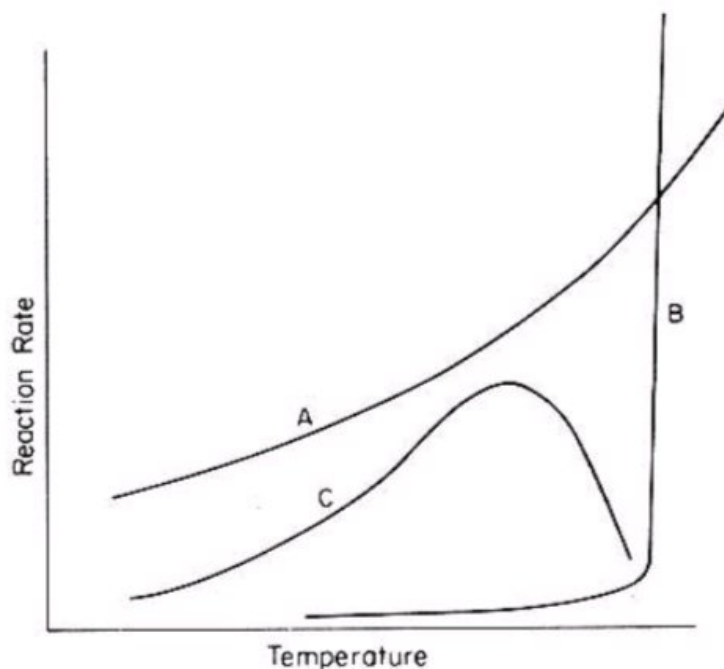


FIGURE 3.10. Typical effects of temperature on reaction rates of (A) inorganic reactions, (B) explosive reactions, and (C) biochemical reactions.

of curve A is characteristic of inorganic reactions, the rate increases two- or three-fold with each 10°C value, or the increase in reaction rate with a 10°C increase in temperature, $Q_{10} = 2$ to 3. The plot of $\log k$ versus $1/T$ is often linear for such reactions. Such data can yield the activation energy E_a from the Arrhenius equation:

$$\frac{\Delta \log k}{\Delta T} = \frac{E_a}{2.303RT^2} \quad (3.57)$$

Another response of rate to temperature is an explosion, curve B of Fig. 3.10. The reaction rate increases only slowly until a critical temperature is reached, whereupon the rate approaches infinity.

A3.3.3 Microbially Catalyzed Reactions

Many chemical reactions in soils occur at measurable rates only because of enzymatic or microbial catalysis. Curve C of Fig. 3.10 is characteristic of biological reactions. Biological reactions generally increase about threefold per 10°C rise in temperature ($Q_{10} = 3$) up to an optimum temperature and then decrease rapidly at higher temperatures. Most soil organisms are *mesophiles*, whose optimal temperatures are 30 to 37°C ; 37°C is particularly common. Soils also contain *thermophiles*, whose optimum temperatures are 55 to 60°C , and *psychrophiles*, whose optimal range is 5 to 15°C . Psychrophiles were once thought to be rare in soils, but recent work suggests that their incidence and importance has been underestimated. The mean annual temperature of most soils is in the 5 to 15°C range.

When biochemical reactions are studied with time, two situations commonly occur. One is when enzyme concentrations remain constant (the biological population

in effect remains constant), and Michaelis–Menten kinetics often apply. This treatment assumes that the enzyme (E) and the reactant or substrate (S) form a complex (ES) that dissociates either to the original substrate and the enzyme, or to a new product (P) and the enzyme. Thus,



Michaelis and Menten found that the rate of substrate disappearance with time could be expressed as

$$-\frac{\Delta[S]}{\Delta t} = \frac{k_3[E][S]}{K_m + [S]} \quad (3.59)$$

where the brackets indicate concentrations and where K_m is the Michaelis constant. Equation 3.59 describes the curve of Fig. 3.11a. Equation 3.59 assumes that all non-specified rate factors are at steady state during the period of measurement.

When the substrate concentration is much smaller than K_m , the denominator of Eq. 3.59 reduces to K_m and the reaction rate, at constant enzyme concentration, is first order with respect to the substrate concentration [S]:

$$-\frac{\Delta[S]}{\Delta t} = \frac{k_3}{K_m[E][S]} = k'[S] \quad (3.60)$$

This equation describes the steep portion of the curve near the origin in Fig. 3.11a. When [S] is much larger than K_m , Eq. 3.60 reduces to

$$-\frac{\Delta[S]}{\Delta t} = k_3[E] \quad (3.61)$$

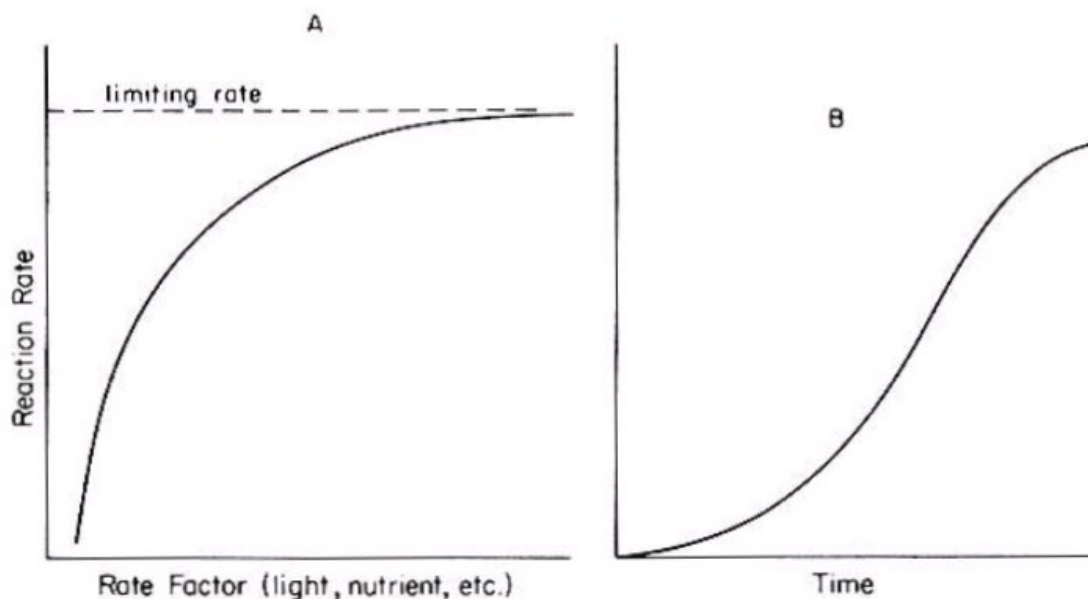


FIGURE 3.11. Change of reaction rate (A) with a rate factor according to the Michaelis–Menten kinetics and (B) with time and population response.

which means that the rate is independent of, or zero order with respect to, S . The rate then depends only on the steady-state concentration of the enzyme, that is, on the plant or microbial population.

The rate of an enzymatic reaction depends on many factors. Increasing one factor generally increases the rate less than the increased amount of the factor, because the rate is now hindered by other growth factors. For instance, nitrogen fertilization may increase crop growth rates, but plants must still contend with limited water and nutrient supplies, disease, and climate. Each successive increment of added nitrogen will have less effect on growth, because other factors are now rate limiting. Only by changing other rate-limiting conditions can an organism take better advantage of an added growth factor. Michaelis–Menten kinetics apply both to short-term, single-plant experiments and to the worldwide plant response to changing P_{CO_2} in the atmosphere. In both cases the population and enzyme concentrations remain constant.

The second situation is more common in experimental work; the biological population increases during the study period in response to some growth factor. This requires time and causes the characteristic lag time before biological reactions begin. This lag distinguishes reactions that are primarily biochemical. Inorganic reactions, in contrast, are usually most rapid at the beginning of the experiment.

During the lag period, the growth of the organism and the corresponding reaction rate are slow but increase exponentially with time. Later the rate slows to zero when a new set of limitations is reached. This results in the familiar S-shaped or sigmoid curve (Fig. 3.11b). The curve is described by equations such as

$$\frac{\Delta N}{\Delta t} = \frac{\Delta[S]}{\Delta t} = \frac{rN(N_{\text{lim}} - N)}{N_{\text{lim}}} \quad (3.62)$$

where N is the number of organisms, N_{lim} is the maximum population of organisms, and r is the difference between the organism's coefficients of birth and death rates (or forward and backward reaction rates). Equation 3.62 applies to such situations as the soil's evolution of CO_2 from freshly introduced organic matter, and the appearance of nitrate in soils recently fertilized with ammonium salts.

The application of kinetics and thermodynamics requires a deeper understanding than the brief introduction given here. Although best suited to simple systems, thermodynamics and kinetics are also unexcelled as tools for the understanding of chemical phenomena in nature.

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QUESTIONS AND PROBLEMS

1. What is the pH of 0.1 M HCl, 0.02 M H₂SO₄, 0.1 M acetic acid ($K = (H^+)(Ac^-)/(HAc) = 10^{-5}$), and 0.1 M NH₄OH ($K = (NH_4^+)(OH^-)/(NH_4OH) = 1.8 \times 10^{-5}$)?
2. What is the pH of a solution containing 0.1 M acetic acid and 0.01 M, 0.1 M, or 0.5 M sodium acetate?
3. A solution initially contains 0.1 M NH₄OH and 0.1 M NH₄Cl. Plot the pH change when acid and base are added to this solution. Compare this curve to the pH curve of a NH₄OH solution titrated with HCl. Why are they different?
4. What is the ionic strength of a solution containing 0.015 M Ca²⁺, 0.05 M Na⁺, 0.030 M Cl⁻, 0.02 M SO₄²⁻, and 0.01 M HCO₃⁻? What are the activity coefficients of the ions in this mixture?
5. What is the aqueous concentration of H₂CO₃ plus CO_{2aq} in equilibrium with air? In equilibrium with a soil atmosphere of $P_{CO_2} = 0.1$? What are the concentrations of HCO₃⁻ and CO₃²⁻ in equilibrium with $P_{CO_2} = 0.1$ at pH 6, 7, and 8?
6. Convert the following values to SI units:
 - (a) 10 meq/100 g
 - (b) 2 mmho/cm
 - (c) 100 kg/ha-yr
 - (d) 150 lb/acre
 - (e) 9 millimicrons
 - (f) 7.4 A
 - (g) 10 me/100 g
7. Calculate the ΔG change during the change from feldspar to gibbsite, soluble silica, and K⁺ (all components in their standard states). What is the further ΔG change if all the activities of soluble silica and K⁺ are 10^{-4} ?
8. The (Al)(PO₄) solubility product of variscite is about 10^{-21} . Calculate the ΔG of the reaction of soluble silica with variscite to form kaolinite at standard conditions and at $Si(OH)_{4aq} = 10^{-4}$.
9. Give the expression for the solubility product and complex stability constant of the hypothetical substance MA. Why do the two expressions differ? When is that assumption invalid?
10. The tendency of minerals is to go to the lowest possible energy state. Why, then, are soils, which are metastable, formed?
11. Describe the stepwise process of changes in water when an ion enters an aqueous solution. What are the two major characteristics of an ion that govern the ion's interaction with water?

12. What effect does one ion in solution have on another? How are these effects taken into account?
13. What masses of which salts would be required to produce 1 L of the solution in Problem 4 (assume the salts are water-free)?
14. Calculate (a) the activity of Fe^{3+} in equilibrium with $\text{Fe}(\text{OH})_3$ at pH 7 and (b) the activity of FeEDTA^- in equilibrium with $\text{Fe}(\text{OH})_3$ at pH 7 if 0.01 M H_4EDTA was added to the solution.
15. Calculate the pH in (a) a 0.005 M solution of HCl, and (b) a 0.005 M solution of acetic acid. Explain why the pH values are different.
16. For a pesticide initially present at a concentration of 25 mg/kg of soil and having a half-life of approximately 15 days under the present field conditions, what concentration of the pesticide will remain after 110 days?