

CHAPTER 6: AQUATIC CHEMISTRY

6.1 INTRODUCTION

Water continually transforms the surface of the Earth, through interaction with the solid surface and transport of dissolved and suspended matter. Beyond that, water is essential to life and central to human activity. Thus as a society, we are naturally very concerned with water quality, which in essence means water chemistry. Aquatic chemistry is therefore the principal concern of many geochemists.

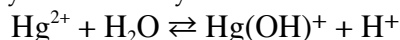
In this chapter, we learn how the tools of thermodynamics and kinetics are applied to water and its dissolved constituents. We develop methods, based on the fundamental thermodynamic tools already introduced, for predicting the species present in water at equilibrium. We then examine the interaction of solutions with solids through precipitation, dissolution, and adsorption.

Most reactions in aqueous solutions can be placed in one of the following categories:

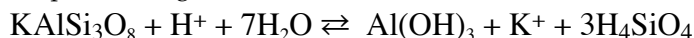
- Acid-base, e.g., dissociation of carbonic acid:



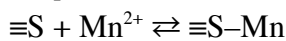
- Complexation, e.g., hydrolysis of mercury:



- Dissolution/Precipitation, e.g., dissolution of orthoclase:



- Adsorption/Desorption, e.g., adsorption of Mn on a clay surface:



(where we are using $\equiv\text{S}$ to indicate the surface of the clay).

In this chapter, we will consider these in detail. We return to the topic of aquatic chemistry in Chapter 13, we examine the weathering process, that is reaction of water and rock and development of soils, and the chemistry of streams and lakes.

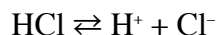
6.2 ACID-BASE REACTIONS

The hydrogen and hydroxide ions are often participants in all the foregoing reactions. As a result, many of these reactions are pH dependent. In order to characterize the state of an aqueous solution, e.g., to determine how much CaCO_3 a solution will dissolve, the complexation state of metal ions, or the redox state of Mn, the first step is usually to determine pH. On a larger scale, weathering of rock and precipitation of sediments depend critically on pH. Thus pH is sometimes called the *master variable* in aquatic systems. We note in passing that while pH represents the hydrogen ion, or proton concentration, the hydroxide ion concentration is easily calculated from pH since the proton and hydroxide concentrations are related by the dissociation constant for water, i.e., by:

$$K_w = a_{\text{H}^+} a_{\text{OH}^-} \quad 6.01$$

The value of K_w , like all equilibrium constants, depends on temperature, but is 10^{-14} at 25°C .

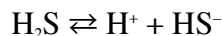
Arrhenius defined an *acid* as a substance that upon solution in water releases free protons. He defined a *base* as a substance that releases hydroxide ions in solution. These are useful definitions in most cases. However, chemists generally prefer the definition of Brønsted, who defined acid and base as proton donors and proton acceptors respectively. The strength of an acid or base is measured by its tendency to donate or accept protons. The dissociation constant for an acid or base is the quantitative measure of this tendency and thus is a good indication of its strength. For example, dissociation of HCl:



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has a dissociation constant:
$$K_{HCl} = \frac{a_{H^+} a_{Cl^-}}{a_{HCl}} = 10^3$$

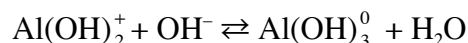
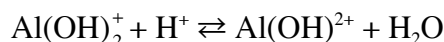
HCl is a strong acid because only about 3% of the HCl molecules added will remain undissociated. The equilibrium constant for dissociation of hydrogen sulfide:



is:
$$K_{H_2S} = \frac{a_{H^+} a_{HS^-}}{a_{H_2S}} = 10^{-7.1}$$

Thus H_2S is a weak acid because very few of the H_2S molecules actually dissociate except at high pH.

Metal hydroxides can either donate or accept protons, depending on pH. For example, we can represent this in the case of aluminum as:



Compounds that can either accept or donate protons are said to be *amphoteric*.

Metals dissolved in water are always surrounded by solvation shells. The positive charges of the hydrogens in the surrounding water molecules are to some extent repelled by the positive charge of the metal ion. For this reason, water molecules in the solvation shell are more likely to dissociate and give up a proton more readily than other water molecules. Thus the concentration of such species will affect pH.

Most protons released by an acid will complex with water molecules to form hydronium ions, H_3O^+ or even $H_5O_2^+$. However, in almost all cases we need not concern ourselves with this and can treat the H^+ ion as if it were a free species. Thus we will use $[H^+]$ to indicate the concentration of $H^+ + H_3O^+ + H_5O_2^+ + \dots$

6.2.1 Proton Accounting, Charge Balance, and Conservation Equations

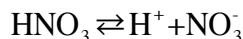
6.2.1.1 Proton Accounting

Knowing the pH of an aqueous system is the key to understanding it and predicting its behavior. This requires a system of accounting for the H^+ and OH^- in the system. There are several approaches to doing this. One such approach is the *Proton Balance Equation* (e.g., Pankow, 1991). In this system, both H^+ and OH^- are considered components of the system, and the proton balance equation is written such that *the concentration of all species whose genesis through reaction with water caused the production of OH^- are written on one side, and the concentration of all species whose genesis through reaction with water caused the production of H^+ are written on the other side*. Because water dissociates to form one H^+ and one OH^- , $[H^+]$ always appears on the left side and OH^- always appears on the right side of the proton balance equation. The proton balance equation for pure water is thus:

$$[H^+] = [OH^-] \quad 6.02^\dagger$$

Thus in pure water the concentrations of H^+ and OH^- are equal.

Now, consider the example of a nitric acid solution. H^+ will be generated both by dissociation of water and dissociation of nitric acid:



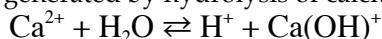
Since one NO_3^- ion is generated for every H^+ , the proton balance equation becomes:

$$[H^+] = [OH^-] + [NO_3^-] \quad 6.03$$

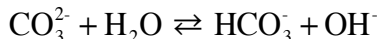
[†] Be careful not to confuse algebraic expressions, written with an equal sign, such as the proton balance equation, with chemical reactions, written with the reaction symbol, \rightleftharpoons . In this case, it is obvious that this is not a balanced chemical reaction, but that will not always be the case.

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Next consider a solution of calcium carbonate. We specify the calcium and carbonate ions as components. Hydrogen ions may be generated by hydrolysis of calcium:



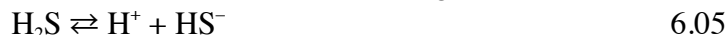
and hydroxide ions may be generated by:



The proton balance equation for this reaction is:

$$[\text{H}^+] + [\text{HCO}_3^-] = [\text{OH}^-] + [\text{Ca}(\text{OH})^+] \quad 6.04$$

Now consider a solution of a *diprotic* acid such as H_2S . H_2S can undergo 2 dissociation reactions:



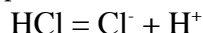
For every HS^- ion produced by dissociation of H_2S , one H^+ ion would have been produced. For every S^{2-} ion, however, 2 H^+ would have been produced, one from the first dissociation and one from the second. The proton balance equation is thus:

$$[\text{H}^+] = [\text{OH}^-] + [\text{HS}^-] + 2[\text{S}^{2-}] \quad 6.07$$

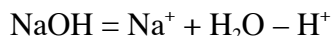
An alternative approach to the proton balance equation is the *TOTH proton mole balance equation* used by Morel and Hering (1993). In this system, H^+ and H_2O are always chosen as components of the system but OH^- is not. The species OH^- is the algebraic sum of H_2O less H^+ :

$$\text{OH}^- = \text{H}_2\text{O} - \text{H}^+ \quad 6.08$$

An implication of this selection of components is that when an acid, such as HCl is present, we choose the conjugate anion as the component, so that the acid, HCl is formed from components:



For bases, such as NaOH , we choose the conjugate cation as a component. The base, NaOH is formed from components as follows:



Because aquatic chemistry almost always deals with dilute solutions, the concentration of H_2O may be considered fixed at a mole fraction of 1, or 55.4 M. Thus in the Morel and Hering system, H_2O is made an *implicit* component, i.e., its presence is assumed but not written, so that equation 6.08 becomes:

$$\text{OH}^- = -\text{H}^+ \quad 6.90$$

The variable *TOTH* is the total amount of component H^+ , rather than the total of species H^+ . Every species containing the component H^+ contributes positively to *TOTH* while every species formed by subtracting component H^+ contributes negatively to *TOTH*. Because we create the species OH^- by subtracting component H^+ from component H_2O , the total of component H^+ for pure water will be:

$$\text{TOTH} = [\text{H}^+] - [\text{OH}^-]$$

Thus *TOTH* in this case is the difference between the concentrations of H^+ and OH^- . Of course, in pure water, $[\text{H}^+] = [\text{OH}^-]$, so *TOTH* = 0.

Now let's consider our example of the CaCO_3 solution. In addition to H^+ and H_2O , we choose Ca^{2+} and CO_3^{2-} as components. In the proton mole balance equation, HCO_3^- counts positively (since $\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+$) and CaOH^+ (since $\text{CaOH}^+ = \text{Ca}^{2+} + \text{H}_2\text{O} - \text{H}^+$) negatively:

$$\text{TOTH} = [\text{H}^+] + [\text{HCO}_3^-] - [\text{OH}^-] - [\text{Ca}(\text{OH})^+] \quad 6.10$$

Comparing equations 6.10 and 6.4, we see that the *TOTH* is equal to the difference between the left and right hand sides of the proton balance equation, and that in this case *TOTH* = 0. This makes sense, because, having added neither $[\text{H}^+]$ nor $[\text{OH}^-]$ to the solution, the total of the component H the solution contains should be 0.

Now consider the dissolution of CO_2 in water to form carbonic acid:

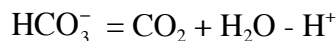


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Under the right conditions of pH, this carbonic acid will dissociate to form bicarbonate ion:



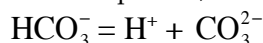
If we choose CO_2 as our component, bicarbonate ion would be made from components CO_2 , H_2O , and H^+ :



Thus in the *TOTH* proton mole balance equation, bicarbonate ion would count negatively, so *TOTH* is:

$$\text{TOTH} = [\text{H}^+] - [\text{OH}^-] - [\text{HCO}_3^-] \quad 6.13$$

Alternatively, had we defined CO_3^{2-} as a component, then species HCO_3^- is formed by the components:



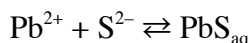
In this case, the proton mole balance equation is:

$$\text{TOTH} = [\text{H}^+] - [\text{OH}^-] + [\text{HCO}_3^-] \quad 6.13a$$

Here we see that *TOTH* depends on how we define our components.

6.2.1.3 Conservation Equations

A further constraint on the composition of a system is provided by *mass balance*. Acid-base reactions will not affect the total concentration of a substance. Thus regardless of reactions 6.5 and 6.6, and any other complexation reactions, such as



the total concentration of sulfide remains constant. Thus we may write:

$$\Sigma \text{S} = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}] + [\text{PbS}_{\text{aq}}] + \dots$$

We can write one mass balance, or *conservation*, equation for each component in solution. Of course for components, such as Na, that form only one species, Na^+ in this case, the mass balance equation is trivial. Mass balance equations are useful for those components forming more than one species.

While the charge balance constraint is an absolute one and always holds, mass balance equations can be trickier because other processes, such as a redox, precipitation, and adsorption, can affect the concentration of a species. We sometimes get around this problem by writing the mass balance equation for an element, since an elemental concentration is not changed by redox processes. We might also define our system such that it is closed to get around the other problems. Despite these restrictions, mass balance often provides a useful additional constraint on a system.

6.2.1.2 Charge Balance

As we saw in Chapter 3, solutions are electrically neutral; that is, the number of positive and negative charges must balance:

$$\boxed{\sum_i m_i z_i = 0} \quad 6.14$$

where m is the number of moles of ionic species i and z is the charge of species i . Equation 6.14 is known as the *charge balance equation* and is identical to equation 3.99. This equation provides an important constraint on the composition of a system. Notice that in some cases, the proton balance and charge balance equations are identical (e.g., equations 6.2 and 6.7).

For each acid-base reaction an equilibrium constant expression may be written. By manipulating these equilibrium constant expressions as well as proton balance, charge balance, and mass balance equations, it is possible to predict the pH of any solution. In natural systems where there are many species present, however, solving these equations can be a complex task indeed. An important step in their solution is to decide which reactions have an insignificant effect on pH and neglect them.

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6.2.3 The Carbonate System

We now turn our attention to carbonate. Water at the surface of the Earth inevitably contains dissolved CO_2 , either as a result of equilibration with the atmosphere or because of respiration by organisms. CO_2 reacts with water to form *carbonic acid*:



Some of the carbonic acid dissociates to form bicarbonate and hydrogen ions:



Some of the bicarbonate will dissociate to an additional hydrogen ion and a carbonate ion:



We can write three equilibrium constant expressions for these reactions:

$$K_{sp} = \frac{a_{\text{H}_2\text{CO}_3}}{f_{\text{CO}_2}} \quad 6.18$$

$$K_1 = \frac{a_{\text{H}^+} a_{\text{HCO}_3^-}}{a_{\text{H}_2\text{CO}_3}} \quad 6.19$$

$$K_2 = \frac{a_{\text{H}^+} a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}} \quad 6.20$$

The equilibrium constants for these reactions are given in Table 6.1 as a function of temperature.

In the above series of reactions, we have simplified things somewhat and have assumed that dissolved CO_2 reacts completely with water to form H_2CO_3 . This is actually not the case, and much of the dissolved CO_2 will actually be present as distinct molecular species, $\text{CO}_{2(\text{aq})}$. Thus reaction 6.15 actually consists of the two reactions:



The equilibrium for the second reaction favors $\text{CO}_{2(\text{aq})}$. However, it is analytically difficult to distinguish between the species $\text{CO}_{2(\text{aq})}$ and H_2CO_3 . For this reason, $\text{CO}_{2(\text{aq})}$ is often combined with H_2CO_3 when representing the aqueous species. The combined total concentration of $\text{CO}_{2(\text{aq})} + \text{H}_2\text{CO}_3$ is sometimes written as H_2CO_3^* . We will write it simply as H_2CO_3 .

The importance of the carbonate system is that by dissociating and providing hydrogen ions to solution, or associating and taking up free hydrogen ions, *it controls the pH of many natural waters*. Example

Table 6.01. Equilibrium Constants for the Carbonate System

T (°C)	$\text{pK}_{\text{CO}_2}^{\text{E}}$	pK_1	pK_2	pK_{cal}	pK_{arag}	$\text{pK}_{\text{CaHCO}_3^+}^*$	$\text{pK}_{\text{CaCO}_3^0}^\dagger$
0	1.11	6.58	10.63	8.38	8.22	-0.82	-3.13
5	1.19	6.52	10.55	8.39	8.24	-0.90	-3.13
10	1.27	6.46	10.49	8.41	8.26	-0.97	-3.13
15	1.34	6.42	10.43	8.43	8.28	-1.02	-3.15
20	1.41	6.38	10.38	8.45	8.31	-1.07	-3.18
25	1.47	6.35	10.33	8.48	8.34	-1.11	-3.22
30	1.52	6.33	10.29	8.51	8.37	-1.14	-3.27
45	1.67	6.29	10.20	8.62	8.49	-1.19	-3.45
60	1.78	6.29	10.14	8.76	8.64	-1.23	-3.65
80	1.90	6.34	10.13	8.99	8.88	-1.28	-3.92
90	1.94	6.38	10.14	9.12	9.02	-1.31	-4.05

* $\text{K}_{\text{CaHCO}_3^+} = a_{\text{CaHCO}_3^+} / (a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-})$

† $\text{K}_{\text{CaCO}_3^0} = a_{\text{CaCO}_3^0} / (a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}})$

^Epressure in units of bars.

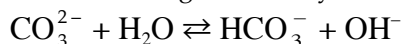
Example 6.01. Proton, Mass, and Charge Balance Equations for Na₂CO₃ Solution

Write the proton, proton mass balance, charge balance, and carbonate conservation equations for a solution prepared by dissolving Na₂CO₃ in water. Assume that NaCO₃ dissociates completely and that the system is closed.

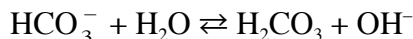
Answer: We begin with the proton balance equation. From the dissociation of water we have:

$$[H^+] = [OH^-]$$

In addition to this, hydroxide ions will also be generated by reaction between CO₃²⁻ and water:



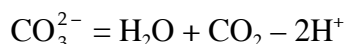
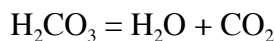
and



Since for each HCO₃⁻ formed, one OH⁻ must have formed and for each H₂CO₃ present two OH⁻ must have formed, the proton balance equation is:

$$[H^+] + [HCO_3^-] + 2[H_2CO_3] = [OH^-] \tag{6.21}$$

Choosing CO₂ and sodium ions as components (in addition to H⁺ and H₂O), the three carbonate species are made from components as follows:



In this case, the proton mole balance equation is:

$$TOTH = [H^+] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] \tag{6.22}$$

The charge balance equation is:

$$[H^+] + [Na^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \tag{6.23}$$

The conservation equation for carbonate species is:

$$\Sigma CO_3 = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] \tag{6.24}$$

Since the dissolution of Na₂CO₃ produces two moles of Na⁺ for every mole of carbonate species, we may also write:

$$[Na^+] = 2\Sigma CO_3 = 2([CO_3^{2-}] + [HCO_3^-] + [H_2CO_3])$$

6.02 shows that pure water in equilibrium with atmospheric CO₂ will be slightly acidic. The production of free H⁺ ions as a result of the solution of CO₂ and dissociation of carbonic acid plays an extremely important role in weathering.

Ground waters may not be in equilibrium with the atmosphere, but will nonetheless contain some dissolved CO₂. Because of respiration of organisms in soil (mainly plant roots & bacteria) through which they pass before penetrating deeper, ground waters often contain much more CO₂ than water in equilibrium with the atmosphere. In addition, calcite and other carbonates are extremely common minerals in soils and in sedimentary, metamorphic, and altered igneous rocks. Ground waters will tend to approach equilibrium with calcite by either dissolving it or precipitating it:

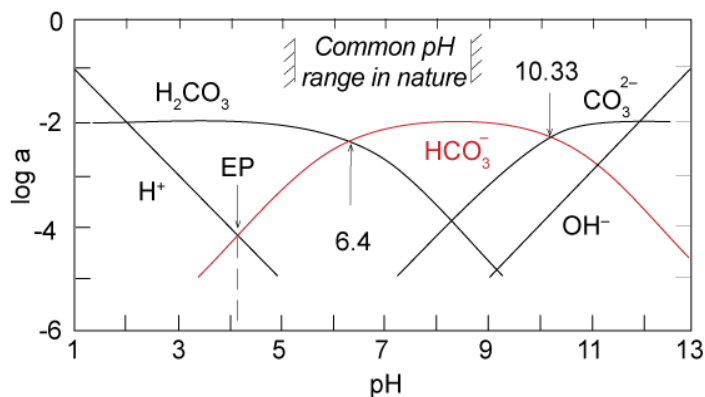


Figure 6.01. Activities of different species in the carbonate system as a function of pH assuming $\Sigma CO_2 = 10^{-2}$. After Drever (1988).

Example 6.02. pH of Water in Equilibrium with the Atmosphere

What is the pH of water in equilibrium with the atmospheric CO₂ at 25°C, assuming ideal behavior and no other dissolved solids or gases present? The partial pressure of CO₂ in the atmosphere is 3.7×10^{-4} .

Answer: In this case, the proton balance and charge balance equations are identical:

$$[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad 6.25$$

We might guess that the pH of this solution will be less than 7 (i.e., $[\text{H}^+] > 10^{-7}$). Under those circumstances, the concentrations of the hydroxyl and carbonate ions will be much lower than that of the hydrogen and bicarbonate ions. Assuming we can neglect them, our equation then becomes simply:

$$[\text{H}^+] \cong [\text{HCO}_3^-] \quad 6.25a$$

We can combine equations 6.18 and 6.19 to obtain an expression for bicarbonate ion in terms of the partial pressure of CO₂:

$$[\text{HCO}_3^-] = (K_1 K_{\text{CO}_2} P_{\text{CO}_2}) / [\text{H}^+]$$

Substituting this into 6.25a and rearranging, we have:

$$[\text{H}^+]^2 \cong K_1 K_{\text{CO}_2} P_{\text{CO}_2} \quad 6.26$$

Taking the negative log of this expression and again rearranging, we obtain:

$$\text{pH} \cong \frac{-\log K_1 - \log K_{\text{CO}_2} - \log P_{\text{CO}_2}}{2}$$

Substituting values from Table 6.1, we calculate pH = 5.64. Looking at Figure 6.1, we can be assured that our assumption that carbonate and hydroxyl ion abundances are valid. Indeed, an exact solution using the Solver in Excel™ differs from the approximate one by less than 0.0001 pH units.



Carbonate ions produced in this way will associate with hydrogen ions to form bicarbonate as in reaction 6.17 above, increasing the pH of the solution. Water containing high concentrations of calcium (and magnesium) carbonate is referred to as 'hard water'; such waters are generally somewhat alkaline.

Now suppose we have a known activity of all carbonate species in solution, say for example 10^{-2} :

$$a_{\text{H}_2\text{CO}_3} + a_{\text{HCO}_3^-} + a_{\text{CO}_3^{2-}} = \Sigma \text{CO}_2 = 10^{-2} \quad 6.28$$

From this, and the dissociation constants, we can calculate the amount of each species present as a function of pH and temperature. For example, we can use the equilibrium constant expressions to obtain substitutions for the carbonic acid and carbonate ion activities in equation 6.28 that are functions of bicarbonate ion activity and pH. We then solve equation 6.28 to obtain an expression for the activity of the bicarbonate ion as a function of total CO₂ and hydrogen ion activity:

$$a_{\text{HCO}_3^-} = \frac{\Sigma \text{CO}_2}{(a_{\text{H}^+} / K_1) + 1 + (K_2 / a_{\text{H}^+})} \quad 6.29$$

Similar equations may be found for carbonic acid and carbonate ion. Carrying out these calculations at various pH, we can construct the graph shown in Figure 6.1. In this figure, we see that carbonic acid is the dominant species at low pH, bicarbonate at intermediate pH, and carbonate at high pH.

6.2.3.1 Equivalence Points

Particularly simple relationships occur when the activities of two species are equal. The pH where this occurs, known as an equivalence point, is determined by equations 6.19 and 6.20. For example, the point where carbonic acid concentration equals bicarbonate concentration can be determined by rearranging equation 6.19:

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$$\frac{a_{\text{HCO}_3^-}}{a_{\text{H}_2\text{CO}_3}} = \frac{K_1}{a_{\text{H}^+}} = 1 \quad 6.30a \quad \text{and therefore:} \quad a_{\text{H}^+} = K_1 = 10^{-6.35} \quad 6.30b$$

The point labeled EP on Figure 6.01 is called the CO_2 equivalence point. At this point, the concentration of the carbonate ion is extremely low, and there is exactly enough H^+ to convert all HCO_3^- to H_2CO_3 . From the perspective of the proton balance then, the HCO_3^- concentration is equivalent to the same concentration of H_2CO_3 . In a similar way, the point where the carbonic acid and carbonate ion concentrations are equal is called the *bicarbonate equivalence point*, and that where bicarbonate and hydroxyl concentrations are equal is called the *carbonate equivalence point*.

The exact concentrations of carbonate species depends on total carbonate concentration as well as the concentration of other ions in solution. Thus the distribution shown in Figure 6.1 is unique to the conditions specified ($\Sigma\text{CO}_2 = 10^{-2}$, no other ions present). Nevertheless, the distribution will be qualitatively similar for other conditions.

6.2.4 Conservative and Non-Conservative Ions

We can divide dissolved ions into *conservative* and *non-conservative* ones. The conservative ions are those whose concentrations are not affected by changes in pH, temperature, and pressure, *assuming no precipitation or dissolution*. In natural waters, the principal conservative ions are Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and NO_3^- . These ions are conservative because they are fully dissociated from their conjugate acids and bases over the normal range of pH of natural waters. Non-conservative ions are those that will undergo association and dissociation reactions in this pH range. These include the proton, hydroxyl, and carbonate species as well as $\text{B}(\text{OH})_4^-$, H_3SiO_4^- , HS^- , NH_4OH , phosphate species, and many organic anions. Virtually all the non-conservative species are anions, the two principle exceptions being H^+ and NH_4OH (which dissociates to form NH_4^+ at low pH). Variations in the concentrations of non-conservative ions result from reactions between them, and these reactions can occur in the absence of precipitation or dissolution. For example, reaction of the carbonate and hydrogen ion to form bicarbonate will affect the concentrations of all three ions. Of course, if the system is at equilibrium, this reaction will not occur in the absence of an external disturbance, such as a change in temperature.

6.2.5 Total Alkalinity and Carbonate Alkalinity

Alkalinity is a measure of acid-neutralizing capacity of a solution and is defined as the sum of the con-

Example 6.03. pH of a Solution with Fixed Total Carbonate Concentration

A groundwater moving through soil into a deep aquifer acquires a total dissolved CO_2 concentration of 10^{-2} M. Assuming the water does not exchange with surrounding rock, ideal behavior and no other dissolved solids or gases, what is the pH of the water?

Answer: In this case, our charge and proton balance equations are the same as in Example 6.2, i.e., equation 6.25. Since the solution does not exchange with surrounding rock, it can be considered a closed system and we can write the following mass balance equation:

$$\Sigma\text{CO}_2 = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 10^{-2} \quad 6.31$$

Simultaneously solving the charge balance and mass balance equations, and using equilibrium constant expressions to eliminate carbonate and OH species, we obtain:

$$[\text{H}^+]^4 + K_1[\text{H}^+]^3 + \{K_2K_1 - K_w - K_1\Sigma\text{CO}_2\}[\text{H}^+]^2 - \{K_w + 2K_2\Sigma\text{CO}_2\}K_1[\text{H}^+] - K_2K_1K_w = 0$$

We might again guess that the concentration of the carbonate ion will be very low, and that we can therefore neglect all terms in which K_2 occurs. We might also guess that pH will be acidic so that $[\text{H}^+] \gg [\text{OH}^-]$, and therefore that we can neglect terms containing K_w . Our equation becomes:

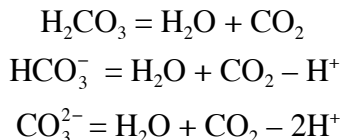
$$K_1^{-1}[\text{H}^+]^2 + [\text{H}^+] = \Sigma\text{CO}_2$$

Solving this quadratic, we find that $\text{pH} = 4.18$.

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centration (in equivalents) of bases that are titratable with strong acid. Mathematically, we define alkalinity as the negative of TOTH when the components are the principal species of the solution at the CO₂ equivalence point. The acidity can be defined as the negative of alkalinity, and hence equal to TOTH.

As a first example, let's consider a solution containing a fixed total dissolved concentration of CaCO₃. At the CO₂ equivalence point, H₂CO₃ is the principal carbonate species, so we choose our components as H⁺, H₂O, CO₂, and Ca²⁺. (Since we always choose water as a component, we do not want to choose H₂CO₃ as a component, because it contains the component H₂O and hence is not fully independent. Instead, we choose CO₂ as the carbonate component in this case). Species H₂CO₃, HCO₃⁻ and CO₃²⁻ are made by combining these components as follows:



The proton mole balance equation is then:

$$\text{TOTH} = [\text{H}^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-] \tag{6.32}$$

The alkalinity is then:

$$\text{Alk} = -\text{TOTH} = -[\text{H}^+] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \tag{6.33}$$

This sum, $-[\text{H}^+] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{OH}^-]$, is called the *carbonate alkalinity*. In this example, carbonate alkalinity and alkalinity are equal since there are no other ions in solution. To avoid confusion with carbonate alkalinity, alkalinity is sometimes called *total alkalinity*.

EXAMPLE 6.4. THE TABLEAU METHOD OF MOREL AND HERING

Write an expression for the alkalinity of a solution containing H₃SiO₄⁻, H₄SiO₄, B(OH)₃, B(OH)₄⁻, H₂S, HS⁻, H₂PO₄⁻, HPO₄²⁻, H₂CO₃, HCO₃⁻, and CO₃²⁻, as well, of course, as OH⁻ and H⁺.

Answer: The alkalinity will be the negative of TOTH when the components are the principal species of the solution at the CO₂ equivalence point, so the real problem is just choosing components and defining our species in terms of these. At the CO₂ equivalence point, the principal species will be H₄SiO₄, B(OH)₃, H₂S, H₂PO₄⁻, and H₂CO₃. The problem now is simply defining the species in terms of components. Morel and Hering (1993) propose a method of setting up a Tableau,

Tableau							
	H ⁺	H ₂ O	CO ₂	H ₂ PO ₄ ⁻	H ₄ SiO ₄	B(OH) ₃	H ₂ S
H ⁺	1						
OH ⁻	-1	1					
H ₂ CO ₃		1	1				
HCO ₃ ⁻	-1	1	1				
CO ₃ ²⁻	-2	1	1				
HPO ₄ ²⁻	-1			1			
H ₂ PO ₄ ⁻				1			
H ₃ SiO ₄ ⁻	-1				1		
H ₄ SiO ₄					1		
B(OH) ₄ ⁻	-1	1				1	
B(OH) ₃						1	
H ₂ S							1
HS ⁻	-1						1

Tableau, a table with the components listed across the top and the species listed vertically. Entries in the table are just the stoichiometric coefficients used to define each species in terms of its components. In this case, the tableau will look like that shown above. The first column of tableau shows us what the coefficients will be in our TOTH equation. Our expression for alkalinity will thus be:

$$\begin{aligned} \text{Alk} = -\text{TOTH} &= -\{[\text{H}^+] - [\text{OH}^-] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{HPO}_4^{2-}] \\ &\quad - [\text{H}_3\text{SiO}_4^-] - [\text{B(OH)}_4^-] - [\text{HS}^-]\} \end{aligned} \tag{6.34}$$

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An analytical definition of alkalinity is that it is the quantity of acid that must be added to the solution to bring the pH to the CO₂ equivalence point.

We can also express alkalinity in terms of conservative and non-conservative ions. The charge balance equation, equation 6.14, could be written as:

$$\sum \text{cations (in equivalents)} - \sum \text{anions (in equivalents)} = 0 \quad 6.35$$

This can be expanded to:

$$\sum \text{conserv. cations} - \sum \text{conserv. anions} + \sum \text{non-conserv. cations} - \sum \text{non-conserv. anions} = 0$$

(all in units of equivalents)*. Rearranging, we have:

$$\sum \text{conserv. cations} - \sum \text{conserv. anions} = -\sum \text{non-conserv. cations} + \sum \text{non-conserv. anions} \quad 6.36$$

The right hand side of equation 6.36 is equal to the *alkalinity*. Hence we may write:

$$\text{Alk} = \sum \text{conserv. cations} - \sum \text{conserv. anions} = -\sum \text{non-conserv. cations} + \sum \text{non-conserv. anions} \quad 6.37$$

This equation emphasizes an important point. The difference of the sum of conservative anions and cations is clearly a conservative property, i.e., they cannot be changed except by the addition or removal of components. Since alkalinity is equal to this difference, alkalinity is also a conservative quantity (i.e., independent of pH, pressure and temperature). *Thus total alkalinity is conservative, even though concentrations of individual species are not.*

6.2.5.1 Alkalinity Determination and Titration Curves

If the concentrations of all major conservative ions in a solution are known, the alkalinity can be simply calculated from equation 6.37. It is often useful, however, to determine this independently. This is done, as the definition of alkalinity suggests, through titration. Titration is the process of progressively adding a strong acid or base to a solution until a specified pH, known as an end-point, is reached. In the case of the determination of alkalinity, this end point is the CO₂ equivalence point.

Consider a solution containing a certain concentration of sodium bicarbonate (Na₂CO₃). Because the carbonate ion can act as a proton acceptor, NaCO₃ is a base. We can determine both the alkalinity and the total carbonate concentration of this solution by titrating with a strong acid, such as HCl. Let's examine the chemistry behind this procedure.

For clarity, we make several simplifying assumptions. First, we assume ideal behavior. Second, we assume the system is closed, so that all components are conserved, except for [H⁺] and [Cl⁻], which we progressively add. Third, we assume that the volume of our Na₂CO₃ solution is sufficiently large and our HCl sufficiently concentrated that there is no significant dilution of the original solution. Finally, we assume both Na₂CO₃ and HCl dissociate completely.

The charge balance equation during the titration is:

$$[\text{Na}^+] + [\text{H}^+] = [\text{Cl}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad 6.38$$

Since the Cl⁻ concentration is conservative, it will be equal to the total amount of HCl added. Into equation 6.38, we can substitute the following:

$$[\text{HCO}_3^-] = \frac{K_1[\text{H}_2\text{CO}_3]}{[\text{H}^+]} \quad 6.39a \quad [\text{CO}_3^{2-}] = \frac{K_1K_2[\text{H}_2\text{CO}_3]}{[\text{H}^+]^2} \quad 6.39b \quad \text{and} \quad [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \quad 6.39c$$

Doing so and rearranging yields:

* One *equivalent* of a species is defined as the number of moles multiplied by the charge of the species. Thus one equivalent of CO₃²⁻ is equal to 0.5 moles of CO₃²⁻, but one equivalent of Cl⁻ is equal to 1 mole of Cl⁻. For an acid or base, an equivalent is the number moles of the substance divided by the number of hydrogen or hydroxide ions that can be potentially produced by dissociation of the substance. Thus there are 2 equivalents per mole of H₂CO₃, but 1 equivalent per mole of Na(OH).

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$$[\text{Cl}^-] = [\text{Na}^+] + [\text{H}^+] - \frac{K_1[\text{H}_2\text{CO}_3]}{[\text{H}^+]} - \frac{K_1K_2[\text{H}_2\text{CO}_3]}{[\text{H}^+]^2} - \frac{K_w}{[\text{H}^+]} \quad 6.40$$

We may also write a conservation equation for carbonate species, which is the same as equation 6.24 in Example 6.1. Substituting equations 6.39a and 6.39b into 6.24 and rearranging, we have:

$$[\text{H}_2\text{CO}_3] = \frac{\Sigma\text{CO}_2}{1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1K_2}{[\text{H}^+]^2}} \quad 6.41$$

Substituting this expression into 6.40, we obtain:

$$[\text{Cl}^-] = [\text{Na}^+] + [\text{H}^+] - \frac{\Sigma\text{CO}_2}{[\text{H}^+] + K_1 + K_1K_2/[\text{H}^+]} \left\{ K_1 - \frac{K_1K_2}{[\text{H}^+]} \right\} - \frac{K_w}{[\text{H}^+]} \quad 6.42$$

From stoichiometry, we also know that $\Sigma\text{CO}_2 = 2[\text{Na}^+]$. From this equation we can construct a plot showing how many moles of HCl we must add to achieve a certain pH. We can also use equation 6.39 and similar ones expressing the bicarbonate and carbonate ions as functions of pH to plot the change in the carbonate speciation during the titration. Figure 6.2 shows such a plot for a 0.005 M Na_2CO_3 solution. There are two regions where pH changes rapidly with small additions of HCl. These are the two end-points of the titration. Comparing the titration curve with the speciation curves, we see that the two end-points correspond to the CO_2 and bicarbonate equivalence points.

An analytical definition of alkalinity is its *acid neutralizing capacity when the end-point of the titration is the CO_2 equivalence point* (Morel and Hering, 1993). We had previously defined alkalinity as the negative of *TOTH* when the principal components are those at the CO_2 equivalence point. Let's now show that these definitions are equivalent.

Our *TOTH* expression, written in terms of components at the CO_2 equivalence point, is identical to 6.22:

$$\text{TOTH} = [\text{H}^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-] \quad (6.32)$$

and the charge balance equation (before any HCl is added) is:

$$[\text{Na}^+] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (6.14)$$

Combining the two we have: $\text{TOTH} = -[\text{Na}^+]$

Since the alkalinity is the negative of *TOTH*, it follows that (before the addition of HCl):

$$\text{Alk} = [\text{Na}^+] \quad 6.43$$

We obtain exactly the same result from equation 6.37. It is easy to show that after titrating to the CO_2 equivalence point, the alkalinity is 0. The change in alkalinity is thus equal to the number of equivalents, or moles, of H^+ we have added to the solution. Since at the end point, $[\text{H}^+] = [\text{HCO}_3^-]$ and the concentrations of CO_3^{2-} and OH^- are negligible, our charge balance equation, 6.38, reduces to:

EXAMPLE 6.5. CALCULATING ALKALINITY OF SPRING WATER

Calculate the alkalinity of spring water from Thonon, France, whose analysis is given at right (this is the same analysis as in Problem 3.9).

Answer: We can use equation 6.37 to calculate alkalinity. All the ions listed here are conservative with the exception of HCO_3^- . To calculate alkalinity, we first need to convert the molar concentrations to equivalents; we do so by multiplying the concentration of each species by its charge. We find the sum of conservative anion concentrations to be 0.749 meq (milliequivalents), and that of the conservative cation concentrations to be 6.535 meq. The alkalinity is the difference, 5.786 meq.

Anions	mM	Cations	mM
HCO_3^-	5.436	Ca^{2+}	2.475
SO_4^{2-}	0.146	Mg^{2+}	0.663
NO_3^-	0.226	K^+	0.036
Cl^-	0.231	Na^+	0.223

$$[\text{Na}^+] = [\text{Cl}^-]$$

Comparing this with 6.42, we see that the alkalinity is equal to the amount of HCl added. In the example in Figure 6.02, the equivalence point occurs after the addition of 10 ml of 1M HCl, or a total of 0.01 moles of Cl⁻. (Notice that since small additions of acid result in large changes in pH at the end points, we do not have to determine pH particularly accurately during the titration for an accurate determination of alkalinity.) So the alkalinity is 0.01 equivalents. This is exactly the answer we obtain from 6.41 for 1 liter of 0.005 M Na₂CO₃ since there are 2 moles of Na⁺ for each mole of Na₂CO₃.

By assuming that the concentration of H⁺ contributes negligibly to charge balance, it is also easily shown (Problem 6.2) that at the bicarbonate equivalence point:

$$\Sigma\text{CO}_2 = [\text{Cl}^-] + [\text{OH}^+] \quad 6.44$$

Thus total carbonate is obtained by titrating to the bicarbonate equivalence point (knowing the pH of the end-point allows us to determine the ΣCO₂ exactly; however neglecting the [OH⁻] term in 6.44 results in only a 1% error in the example shown). In Figure 6.2, this occurs after the addition of 5 ml 1M HCl.

6.2.6 Buffer Intensity

The carbonate system is a good example of a pH *buffer*. We define the *buffer intensity* of a solution as the inverse of change in pH per amount of strong base (or acid) added:

$$\beta \equiv \frac{dC_B}{dpH} = -\frac{dC_A}{dpH} \quad 6.45$$

where C_B and C_A are the concentrations, in equivalents, of strong base or acid respectively. The greater the buffer capacity of a solution, the less change in its pH as an acid or base is added. The buffer capacity of a solution can be calculated by differentiation of the equation relating base (or acid) concentration to pH, as is illustrated in Example 6.05.

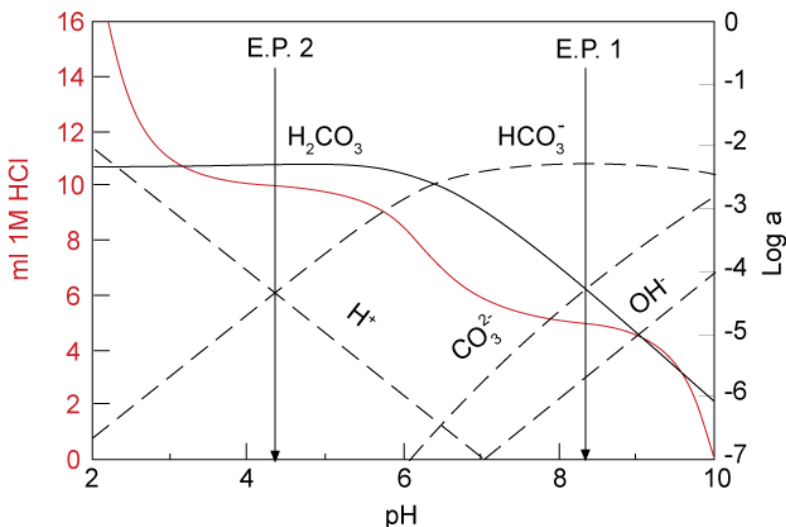


Figure 6.02. Titration curve (solid red line) for a one liter 0.005 M Na₂CO₃ solution titrated with 1M HCl. Left axis shows the number of ml of HCl to be added to obtain a given pH. Also shown are the concentrations of carbonate species, H⁺, and OH⁻ (dashed black lines, right axis gives scale). EP1 is the bicarbonate equivalence point, EP2 is the CO₂ equivalence point.

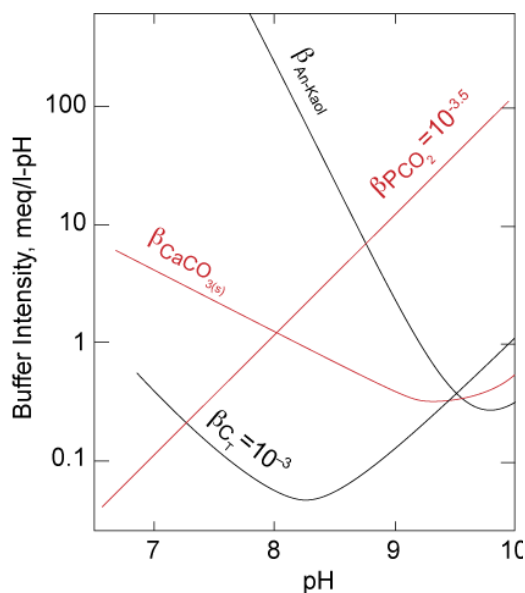


Figure 6.03. Buffer intensity as a function of pH for several ideal natural systems: β_{C_T} fixed total dissolved CO₂, β_{P_{CO₂}} water in equilibrium with atmospheric CO₂, β_{CaCO_{3(s)}} water in equilibrium with calcite, and β_{An-Kaol} water in equilibrium with anorthite and kaolinite. After Stumm and Morgan (1996).

Example 6.06. Calculating Buffer Intensity

How will pH change for given addition of a strong base such as NaOH for a solution of pure water in equilibrium with atmospheric CO₂? Calculate the buffer intensity of this solution as a function of pH. Assume that NaOH completely dissociates and behavior is ideal.

Answer: We want to begin with the charge balance equation in this case because it relates the two quantities of interest in this case, [Na⁺] and [H⁺]. The charge balance equation is the same as in Example 6.1:

$$[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (6.23)$$

Since Na⁺ is a conservative ion, its concentration will depend only on the amount of NaOH added, so that C_B = [Na⁺]. Substituting this into equation 6.14 and rearranging, we have:

$$C_B = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+] \quad 6.46$$

We can now use the equilibrium constant relations to substitute for the first three terms of the right hand side of 6.46 and obtain:

$$C_B = \frac{K_w + K_1 K_{sp} P_{\text{CO}_2}}{[\text{H}^+]} + 2 \frac{K_2 K_1 K_{sp} P_{\text{CO}_2}}{[\text{H}^+]^2} - [\text{H}^+]$$

Using the relation pH = -log [H⁺] to replace [H⁺] in this equation with pH, we have:

$$C_B = \frac{K_w + K_1 K_{sp} P_{\text{CO}_2}}{10^{-\text{pH}}} + 2 \frac{K_2 K_1 K_{sp} P_{\text{CO}_2}}{10^{-2\text{pH}}} - 10^{-\text{pH}}$$

Now differentiating with respect to pH, we obtain:

$$\frac{dC_B}{dpH} = \beta = \ln 10 \left\{ (K_w + K_1 K_{sp} P_{\text{CO}_2}) 10^{\text{pH}} + 4 K_2 K_1 K_{sp} P_{\text{CO}_2} 10^{2\text{pH}} + 10^{-\text{pH}} \right\} \quad 6.47$$

Figure 6.04 shows a plot of this equation using the values in Table 6.01. Buffer intensity is negligible in neutral to slightly acidic conditions, but increases rapidly with pH.

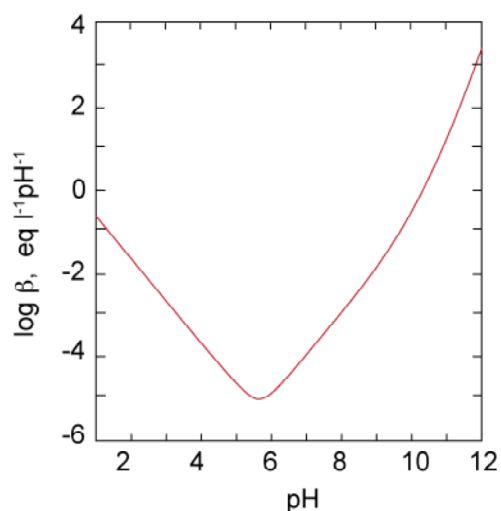


Figure 6.04. Buffer capacity of a carbonate solution in equilibrium with atmospheric CO₂.

A pH buffer acts to control pH within a narrow range as H⁺ ions are added or removed from solution by other reactions. To understand how this works, imagine a solution containing carbonic acid, CO₃²⁻, HCO₃⁻, and H⁺ ions in equilibrium concentrations. Now imagine that additional H⁺ ions are added (for example, by addition of rain water containing HNO₃). In order for the right hand side of equation 6.19 to remain equal to K₁ despite an increase in the activity of H⁺ (which it must at constant temperature and pressure), the bicarbonate activity must decrease and the carbonic acid activity increase. It is apparent then that reaction 6.16 must be driven to the left, taking free hydrogen ions from solution, hence driving the pH back toward its original value. Similarly, reaction 6.20, the dissociation of bicarbonate, will also be driven to the left, increasing the bicarbonate concentration and decreasing the hydrogen and carbonate ion concentrations.

The buffer capacity of the carbonate system depends strongly on pH and also on the concentration of the carbonate species and the concentration of other ions in solution. In pure water containing no other ions and only carbonate in amounts in equilibrium with the atmosphere, the buffering capacity is negligible near neutral pH, as is shown in Figure 6.4. Natural solutions, however, can have substantial buffering capacity. Figure 6.3 illustrates three other examples of natural pH buffers. "Hard water" is an example of water with a substantial buffering capacity due to the presence of dissolved carbonates. As

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we shall see, how adversely lakes and streams are impacted by “acid rain” depends on their buffering intensity.

6.3 COMPLEXATION

Ions in solution often associate with other ions, forming new species called complexes. Complex formation is important because it affects the solubility and reactivity of ions, as we will see in the following section. In some cases, complex formation is an intermediate step in the precipitation process. In other cases, ions form stable, soluble complexes that greatly enhance the solubility of the one or both of the ions.

Complexation is usually described in terms of a central ion, generally a metal, and ions or molecules that surround, or *coordinate*, it, referred to as *ligands*. Perhaps the simplest and most common complexes are those formed between metals and water or its dissociation products. We learned in Section 3.7 that a solvation shell surrounds ions in aqueous solutions. The solvation shell (Figure 3.10) consists of water molecules, typically 6, though fewer in some cases, loosely bound to the ion through electrostatic forces. This solvation shell is referred to as an *aquo complex*. Water molecules are the ligands in aquo-complexes. Aquo-complexes are ubiquitous: all charged species have a solvation shell. Truly “free ions” do not exist: ions not otherwise complexed (“free ions”) are in reality associated with surrounding water molecules and hence actually aquo-complexes. However, the existence of this type of complex is implicitly accounted for through the activity coefficient and not usually explicitly considered. Nevertheless, it is important to bear in mind that since all ions are complexed in some way to begin with, every complexation reaction in aqueous solution is essentially a ligand exchange reaction.

Beyond aquo complexes, we can distinguish two types of complexes:

- *Ion pairs*, where ions of opposite charge associate with one and other through electrostatic attraction, yet each ion retains part or all of its solvation sphere. Figure 6.05 illustrates two possibilities: one where the two solvation spheres are merely in contact, the other where the water molecules are shared between the two solvation spheres. Ion pairs are also called *outer sphere complexes*.

- *Complexes (senso stricto)*, where the two ions are in contact and a bond forms between them that is at least partly covalent in nature (Figure 6.05c). These are often called *inner sphere complexes*.

6.3.1 Stability Constants

In its simplest form, the reaction for the formation of an ion pair or complex between a metal cation M and an anion or ligand L may be written as:



As with any other reaction, we may define an equilibrium constant as:

$$K = \frac{a_{M_m L_\bullet}}{a_M^m a_L^\bullet} \quad 6.48$$

For example, the equilibrium constant for the reaction:

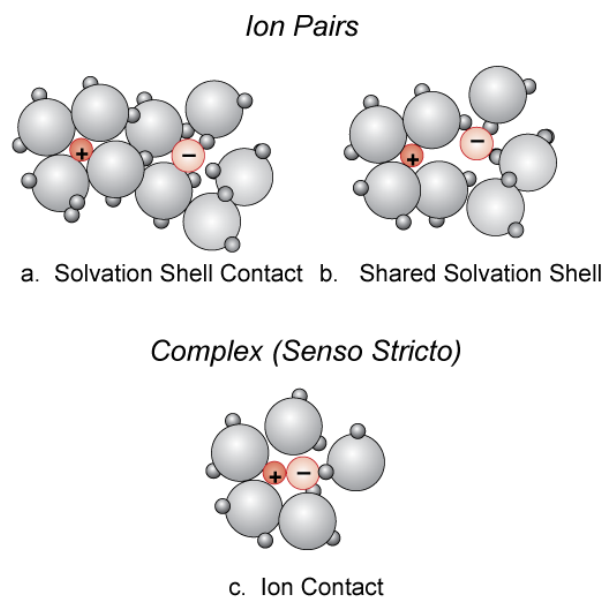
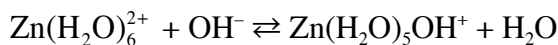


Figure 6.5. Illustration of ion pair and complex formation. Two types of ion pairs can be envisioned: (a) solvation shell contact and (b) solvation shell sharing. Ion pairs are sometimes referred to as outer sphere complexes. In formation of true complexes, ions are in contact (c) and there is some degree of covalent bonding between them. These are sometimes referred to as inner sphere complexes.

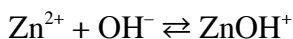
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is:

$$K_1 = \frac{a_{\text{Zn}(\text{H}_2\text{O})_5(\text{OH})^+}}{a_{\text{Zn}(\text{H}_2\text{O})_6^{2+}} a_{\text{OH}^-}}$$

(we omit the activity of water because we assume, as usual, that it is 1). As we noted, however, the aquo-complex is generally not explicitly expressed, so this same reaction would more often be written as:

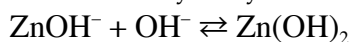


and the equilibrium constant as:

$$\beta_1 = K_1 = \frac{a_{\text{Zn}(\text{OH})^+}}{a_{\text{Zn}^{2+}} a_{(\text{OH})^-}}$$

Equilibrium constants for complex formation reactions are often referred to as *stability constants*, since their value is an indication of the stability of the complex, and often denoted by β . Thus for the reaction above, β_1 and K_1 are synonymous. *By convention, stability constants are written so as the complex appears in the numerator (i.e., as a product of the reaction).*

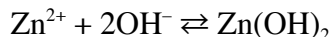
The zinc ion might associate with a second hydroxyl:



The equilibrium constant is:

$$K_2 = \frac{a_{\text{Zn}(\text{OH})_2}}{a_{\text{Zn}(\text{OH})^+} a_{(\text{OH})^-}}$$

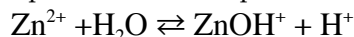
Here, however, the notation for the stability constant and the equilibrium constant differs. Whereas K_2 refers to the reaction above, β_2 refers to the reaction:



Hence:

$$\beta_2 = \frac{a_{\text{Zn}(\text{OH})_2}}{a_{\text{Zn}^{2+}} a_{\text{OH}^-}^2} = K_1 K_2$$

Finally, the notation $*K$ and $*\beta$ are sometimes used for reactions in which the complexation reactions are written so as the hydrogen ion occurs as a product, for example:



and:

$$*K_1 = \frac{a_{\text{Zn}(\text{OH})^+} a_{\text{H}^+}}{a_{\text{Zn}^{2+}}}$$

$*K_1$ is then related to K_1 as: $*K_1 = K_1 K_W = *\beta_1$ where K_W is the water dissociation constant (10^{-14}).

We can define *apparent* equilibrium and stability constants, where the molar concentrations are used in place of activity. Indeed, as in other aspects of geochemistry, apparent equilibrium constants are more commonly encountered than true ones.

The equilibrium constant may in turn be related to the Gibbs Free Energy of the reaction, as in equation 3.86. Interestingly, the

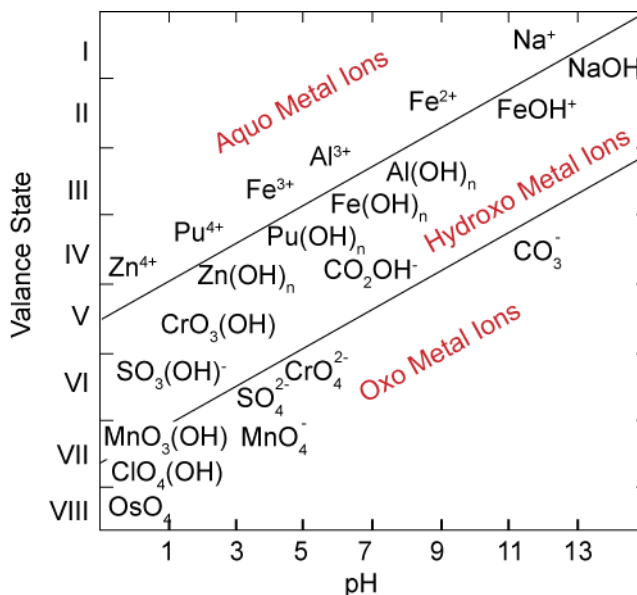


Figure 6.06. Predominant aquo, hydroxo, and oxo complexes as a function of pH and valence state. After Stumm and Morgan (1996).

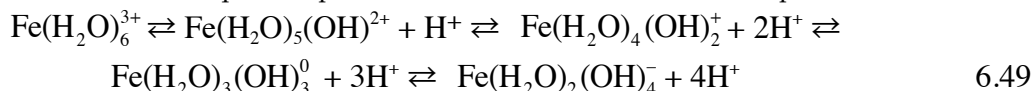
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free energy changes involved in complexation reactions result largely from entropy changes. Indeed, the enthalpy changes of many complexation reactions are unfavorable, and the reaction proceeds only because of large positive entropy changes. These entropy changes result from the displacement of water molecules from the solvation shell.

The link between the equilibrium constant and the free energy change is particularly important and useful in complexation reactions because it is in most instances difficult to determine the concentrations of individual complexes analytically. Thus our knowledge of chemical speciation in natural waters derived largely from predictions based on equilibrium thermodynamics.

6.3.2 Water-Related Complexes

Let's further consider the types of complexes typically found in aqueous solution. Ferric iron, for example, can form a $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ complex. The positive charge of the central ion tends to repel hydrogens in the water molecules, so that water molecules in these aquo-complexes are more readily hydrolyzed than otherwise. Thus these aquo-complexes can act as weak acids. For example:

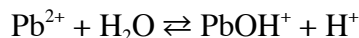


As reaction 6.49 suggests, equilibrium between these *hydroxo-complexes* depends strongly on pH.

The repulsion between the central metal ion and protons in water molecules of the solvation shell will increase with decreasing diameter of the central ion (decreasing distance between the protons and the metal) and with increasing charge of the central ion. For highly charged species, the repulsion of the central ion is sufficiently strong that all hydrogens are repelled and it is surrounded only by oxygens. Such complexes, for example, MnO_4^- and CrO_4^{2-} , are known as *oxo-complexes*. Intermediate types in which the central ion is surrounded, or *coordinated*, by both oxygens and hydroxyls are also possible, for example $\text{MnO}_3(\text{OH})$ and $\text{CrO}_3(\text{OH})^-$, and are known as *hydroxo-oxo complexes*. Figure 6.6 summarizes the predominance of aquo, hydroxo, hydro-oxo, and oxo complexes as a function of pH and valence state. For most natural waters, metals in valence states I and II will be present as "free ions", i.e., aquo complexes, valence III metals will be present as aquo and hydroxo complexes, those with higher charge will present as oxo-complexes.

EXAMPLE 6.7. COMPLEXATION OF Pb

Assuming an equilibrium constant for the reaction:



of $10^{-7.7}$, calculate the fraction of Pb that will be present as PbOH^+ from pH 6 to 9.

Answer: The equilibrium constant expression is:

$$K = \frac{[\text{PbOH}^+][\text{H}^+]}{[\text{Pb}^{2+}]}$$

In addition to the equilibrium constant expression, we also need the conservation equation for Pb:

$$\Sigma \text{Pb} = \text{Pb}^{2+} + \text{PbOH}^+$$

Solving the conservation equation for Pb^{2+} and substituting into the equilibrium constant expression, we obtain:

$$(\Sigma \text{Pb} - [\text{PbOH}^+])K = [\text{PbOH}^+][\text{H}^+]$$

With some rearranging, we eventually obtain the following expression:

$$[\text{PbOH}^+]/\Sigma \text{Pb} = \frac{K}{K + [\text{H}^+]}$$

The result is illustrated in Figure 6.7. Below pH 6, virtually all Pb is present as Pb^{2+} , above pH 9, virtually all Pb is present as PbOH^+ .

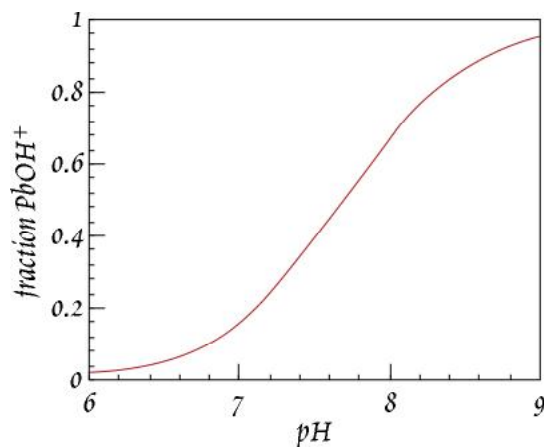
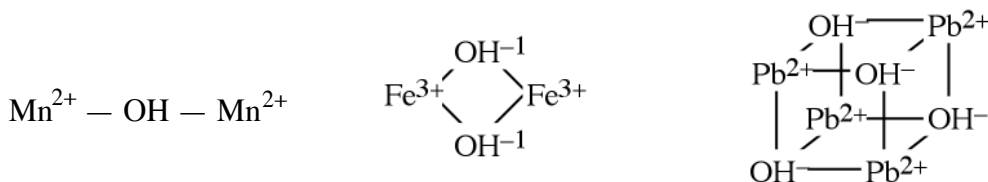


Figure 6.7. Fraction of Pb complexed as PbOH^+ as a function of pH.

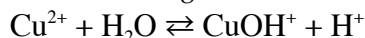
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Polynuclear hydroxo- and oxo-complexes, containing two or more metal ions, are also possible, for example:



As one might expect, the extent to which such *polymeric* species form depends on the metal ion concentration: they become increasingly common as concentration increases. Most highly-charged metal ions (3+ and higher oxidation states) are highly insoluble in aqueous solution. This is due in part to the readiness with which they form hydroxo-complexes, which can in turn be related to the dissociation of surrounding water molecules as a result of their high charge. When such ions are present at high concentration, formation of polymeric species such as those above quickly follows formation of the hydroxo complex. At sufficient concentration, formation of these polymeric species leads to the formation of colloids and ultimately to precipitation. In this sense, these polymeric species can be viewed as intermediate products of precipitation reactions.

Interestingly enough, however, the tendency of metal ions to hydrolyze decreases with concentration. The reason for this is the effect of the dissociation reaction on pH. For example, increasing the concentration of dissolved copper decreases the pH, which in turn tends to drive the hydrolysis reaction to the left. To understand this, consider the following reaction:



for which the apparent equilibrium constant is $K^{\text{app}} = 10^{-8}$. We can express the fraction of copper present as CuOH^+ , α_{CuOH^+} as:

$$\alpha = \frac{[\text{CuOH}^+]}{C_{\text{Cu}}} = \frac{K}{[\text{H}^+] + K} \tag{6.50}$$

where C_{Cu} is the total dissolved copper. At constant pH, the fraction of Cu complexed is constant. However, for a solution with a fixed amount of Cu ion dissolved, we can also write a proton balance equation:

$$[\text{H}^+] = [\text{CuOH}^+] + [\text{OH}^-]$$

and a mass balance equation. Combining these with the equilibrium constant expression, we can calculate both α and pH as a function of C_{Cu} (Problem 6.11). When we do this, we see that as C_{Cu} increases, both pH and α decrease, as is demonstrated in Figure 6.08.

6.3.3 Other Complexes

When non-metals are present in solution, as they would inevitably be in natural waters, then other complexes are possible. In this respect, we can divide the elements into four classes (Table 6.02, Figure 6.09). The first is the non-metals, which form anions or anion groups. The second group is the "A-type" or "hard" metals. These metals, listed in Table 6.02, have spherically symmetric, inert-gas type outer electron configurations. Their electron shells are not readily deformed by electric fields and can be viewed as "hard spheres". Metals in this group preferentially

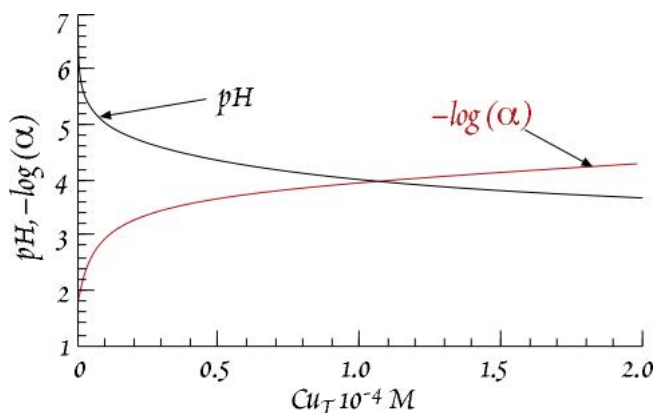


Figure 6.08. pH and $-\log \alpha$, as a function of total copper concentration in aqueous solution. α is the fraction of copper present as the hydroxo-complex.

H																				He
Li	Be											B	C	N	O	F				Ne
Na	Mg											Al	Si	P	S	Cl				Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br				Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I				Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At				Rd
Fr	Ra	Ac																		
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
			Ac	Th	Pa	U	Np	Pu												

A-Metals
 Transition Metals
 B Metals
 Ligand Formers

Figure 6.09. Classification of the elements with respect to complex formation in aqueous solution.

forms complexes with fluorine and ligands having oxygen as the donor atoms (e.g., OH^- , CO_3^{2-} , PO_4^{3-} , SO_4^{2-}). Stability of the complexes formed by these metals increases with charge to radius ratio. Thus the alkalis form only weak, unstable complexes, while elements such as Zr^{4+} form very strong, stable complexes (e.g., with fluorine). In complexes formed by A-type metals, anions and cations are bound primarily by electrostatic forces, i.e., ionic-type bonds. The A-type elements correspond approximately to the lithophile elements of Goldschmidt's classification presented in Chapter 7.

The third group is the B-type, or "soft", metal ions. Their electron sheaths are not spherically symmetric and are readily deformed by the electrical fields of other ions (hence the term soft). They preferentially form complexes with bases having S, I, Br, Cl, or N (such as ammonia; not nitrate) as the donor atom. Bonding between the metal and ligand(s) is primarily covalent and is comparatively strong. Thus Pb form strong complexes with Cl^- and S^{2-} . Many of the complexes formed by these elements are quite insoluble. The B-type elements consist primarily of the "chalcophile elements", a term we will define in the next chapter.

The first series transition metals form the fourth group, and correspond largely to the siderophile elements (see Chapter 7). Their electron sheaths are not spherically symmetric, but they are not so readily polarizable as the B-type metals. On the whole, however, their complex-forming behavior is similar to that of the B-type metals.

Among the transition metals, the sequence of complex stability is $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$, a sequence known as the *Irving-Williams Series*. This is illustrated in Figure 6.10. In that figure, all the sulfate complexes have approximately the same stability, a reflection of the predominantly electrostatic bonding between sul-

Table 6.02. Classification of Metal Ions

A-Type Metals

Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} ,
 Ba^{2+} , Al^{3+} , Sc^{3+} , Y^{3+} , REE, Ti^{4+} , Si^{4+} , Zr^{4+} ,
 Hf^{4+} , Th^{4+} , Nb^{5+} , Ta^{5+} , U^{6+}

B-Type Metals

Cu^{2+} , Ag^+ , Au^+ , Tl^+ , Ga^+ , Zn^{2+} , Cd^{2+} ,
 Hg^{2+} , Pb^{2+} , Sn^{2+} , Tl^{3+} , Au^{3+} , In^{3+} , Bi^{3+}

Transition Metal Ions

V^{2+} , Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} ,
 Cu^{2+} , Ti^{3+} , V^{3+} , Cr^3+ , Mn^{3+} , Fe^{3+} , Co^{3+}

From Stumm and Morgan (1996).

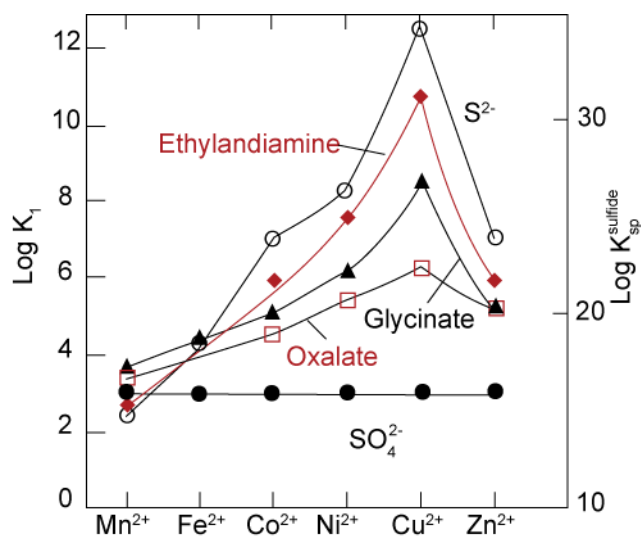


Figure 6.10. Stability constants for transition metal sulfate and organic complexes and their sulfide solubility constants, illustrating the Irving-Williams series. From Stumm and Morgan (1996).

tion, all complexation reactions are ligand exchange reactions: water playing the role of ligand in “free ions”. The rate at which complexes form is thus governed to a fair degree by the rate at which water molecules are replaced in the hydration sphere.

6.3.4 Complexation in Fresh Waters

Where only one metal is involved, the complexation calculations are straightforward, as exemplified in Example 6.7. Natural waters, however, contain many ions. The most abundant of these are Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , and there are many possible complexes between them as well as with H^+ and OH^- . To calculate the speciation state of such solutions an iterative approach is required. The calculation would be done as follows. First, we need the concentrations, activity coefficients, and stability constants (or apparent stability constants) for all species. Then we assume all ions are present as free ions and calculate the concentrations of the various possible complexes on this basis. In this pass, we need only consider the major ions (we can easily understand why with an example: formation of PbCl^+ when the concentration of Pb is 10^{-8} or less and the abundance of Cl^- is 10^{-4} or more will have an insignificant affect on the free ion Cl concentration). We then iterate the calculation, starting with the free ion concentrations corrected for abundances of complexes we calculated in the previous iteration. This process is repeated until two successive iterations produce the same result. Although it sounds difficult, such calculations typically converge within 2 to 4 iterations. Example 6.8 shows how this is done. Once free ion concentrations of the major ligands are known, the speciation of trace metals may be calculated.

As Example 6.8 demonstrates, the major metals in fresh waters are present mainly as free ions (aquo complexes), as are the three most common anions, chloride, sulfate, and bicarbonate. The alkali and alkaline earth trace elements are also largely uncomplexed. Co^{2+} , Ni^{2+} , Zn^{2+} , Ag^+ , and Cd^{2+} are roughly 50% complexed. The remaining metals are present as primarily as complexes. B , V , Cr , Mo , and Re , as well as As and Se are present as anionic oxo-complexes. Other metals are usually present as hydroxide, carbonate, chloride, or organic complexes. Under reducing conditions, HS^- and S^{2-} complexes are important. In organic-rich waters such as swamps, organic complexes can be predominant. We will discuss organic complexes in more detail in Chapter 14, and speciation in seawater in Chapter 15.

fate and metal. Pronounced differences are observed for organic ligands. The figure demonstrates an interesting feature of organic ligands: although the absolute value of stability complexes varies from ligand to ligand, the relative affinity of ligands having the same donor atom for these metals is always similar.

Organic molecules can often have more than one functional group and hence can coordinate a metal at several positions, a process called chelation. Such ligands are called *multi-dentate* and organic compounds having these properties are referred to as chelators or chelating agents. We will explore this topic in greater detail in the Chapter 14.

The kinetics of complex formation is quite fast in most cases, so that equilibrium can be assumed. There are exceptions, however. As we noted earlier in this section,

EXAMPLE 6.8. SPECIATION IN FRESH WATER

Using the water and stability constants given in the adjacent tables, calculate the activities of the major species in this water.

Answer: The first two problems we need to address are the nature of the carbonate species and activity coefficients. At this pH, we can see from Figure 6.1 that bicarbonate will be the dominant carbonate species. Making the initial assumption that all carbonate is bicarbonate, we can calculate ionic strength and activity coefficients using the Debye-Hückel Law (equation 3.74). These are shown in the table below. Having the activity coefficients, we can calculate the approximate abundance of the carbonate ion by assuming all carbonate is bicarbonate:

ANALYSIS OF STREAM WATER (mM)

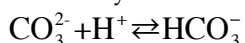
Na ⁺	0.32	Cl ⁻	0.22
K ⁺	0.06	SO ₄ ²⁻	0.12
Mg ²⁺	0.18	ΣCO ₂	1.0
Ca ²⁺	0.36	pH	8.0

LOG STABILITY CONSTANTS

	OH ⁻	HCO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻	Cl ⁻
H ⁺	14	6.35	10.33	1.99	-
Na ⁺	-	-0.25	1.27	1.06	-
K ⁺	-	-	-	0.96	-
Mg ²⁺	2.56	1.16	3.4	2.36	-
Ca ²⁺	1.15	1.26	3.2	2.31	-

$$[CO_3^{2-}] = \frac{\gamma_{HCO_3} \Sigma CO_2}{\beta a_{H^+} \gamma_{CO_3^{2-}}} \tag{6.51}$$

where β is the stability constant for the complexation reaction:



The “corrected” bicarbonate ion is then calculated as:

$$[HCO_3^-] = \Sigma CO_2 - [CO_3^{2-}]$$

The result confirms our initial first order assumption that all carbonate is present as bicarbonate.

Using the concentrations and stability constants given as well as the activity coefficients we calculated, we can then make a first pass at calculating the concentrations of the complexes. For example, MgCO₃ is calculated as

$$a_{MgCO_3} = \beta_{MgCO_3} a_{Mg^{2+}} a_{CO_3^{2-}}$$

The results of this first iteration are shown in a matrix. Chlorine does not complex with any of the major ions to any significant degree, so we can neglect it in our calculations.

We then correct the free ion activities by subtracting the activities of the complexes they form. Thus for example, the corrected free ion activity of Mg²⁺ is calculated as:

$$a_{Mg^{2+}}^{corr} = a_{Mg^{2+}}^{ini} - a_{MgOH^-} - a_{MgHCO_3^-} - a_{MgCO_3} - a_{MgSO_4}$$

We then repeat the calculation of the activities of the complexes using these corrected free ion activities. A second matrix shows the results of this second iteration. A third table shows the percent of each ion present as a free ion (aquo complex). In fresh waters such as this one, most of the metals are present as free ions, the alkaline earths being 5% complexed by sulfate and carbonate.

ION ACTIVITIES: ITERATION 1

	free ion	OH ⁻	HCO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻
free ion		1×10 ⁻⁰⁶	9.17×10 ⁻⁰⁴	6.79×10 ⁻⁰⁷	1.62×10 ⁻⁰⁴
H ⁺	1×10 ⁻⁰⁸	—	2.12×10 ⁻⁰⁵	9.46×10 ⁻⁰⁴	1.75×10 ⁻¹⁰
Na ⁺	3.03×10 ⁻⁰⁴	—	1.62×10 ⁻⁰⁷	2.51×10 ⁻⁰⁸	6.27×10 ⁻⁰⁷
K ⁺	5.69×10 ⁻⁰⁵	—	—	—	9.33×10 ⁻⁰⁸
Mg ²⁺	1.39×10 ⁻⁰⁴	5.09×10 ⁻⁰⁸	2.0310 ⁻⁰⁶	1.65×10 ⁻⁰⁶	6.10×10 ⁻⁰⁶
Ca ²⁺	2.77×10 ⁻⁰⁴	4.29×10 ⁻⁰⁹	5.08×10 ⁻⁰⁶	2.07×10 ⁻⁰⁶	1.08×10 ⁻⁰⁵

ION ACTIVITIES: ITERATION 2

	free ion	OH ⁻	HCO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻
free ion		1×10 ⁻⁰⁶	9.12×10 ⁻⁰⁴	1.12×10 ⁻⁰⁶	1.65×10 ⁻⁰⁴
H ⁺	1×10 ⁻⁰⁸	—	2.06×10 ⁻⁰⁵	9.12×10 ⁻⁰⁴	1.58×10 ⁻¹⁰
Na ⁺	3.03×10 ⁻⁰⁴	—	1.57×10 ⁻⁰⁷	2.35×10 ⁻⁰⁸	5.64×10 ⁻⁰⁷
K ⁺	5.69×10 ⁻⁰⁵	—	—	—	8.40×10 ⁻⁰⁸
Mg ²⁺	1.40×10 ⁻⁰⁴	5.03×10 ⁻⁰⁸	1.84×10 ⁻⁰⁶	1.45×10 ⁻⁰⁶	5.14×10 ⁻⁰⁶
Ca ²⁺	2.80×10 ⁻⁰⁴	3.92×10 ⁻⁰⁹	4.64×10 ⁻⁰⁶	1.83×10 ⁻⁰⁶	9.16×10 ⁻⁰⁶

% FREE ION

Na ⁺	99.76%	Cl ⁻	100%
K ⁺	99.85%	SO ₄ ²⁻	91.7%
Mg ²⁺	94.29%	HCO ₃ ⁻	99.3%
Ca ²⁺	94.71%	CO ₃ ²⁻	25.3%

6.4 DISSOLUTION AND PRECIPITATION REACTIONS

6.4.1 Calcium Carbonate in Ground and Surface Waters

Calcium carbonate is an extremely common component of sedimentary rocks and is present in weathered igneous and metamorphic rocks. It is also a common constituent of many soils. Water passing through such soils and rocks will precipitate or dissolve calcite until equilibrium is achieved. This process has a strong influence on carbonate concentrations, hardness, and pH as well as dissolved calcium ion concentrations. Let's examine calcite solubility in more detail.

The solubility product of calcite is:

$$K_{sp-cal} = a_{Ca^{2+}} a_{CO_3^{2-}} \quad 6.52$$

This can be combined with equations 6.18–20 to obtain the calcium concentration water in equilibrium with calcite as a function of P_{CO_2} :

$$[Ca^{2+}] = P_{CO_2} \frac{K_1 K_{sp-cal} K_{sp-CO_2}}{K_2 \gamma_{Ca^{2+}} \gamma_{HCO_3^-}^2 [HCO_3^-]^2} \quad 6.53$$

In a solution in equilibrium with calcite and a CO_2 gas phase and containing no other dissolved species, it is easy to modify equation 6.53 so that the calcium ion concentration is a function of P_{CO_2} only. A glance at Figure 6.1 shows that we can neglect OH^- , H^+ , and CO_3^{2-} if the final pH is less than about 9. The charge balance equation in this case reduces to:

$$2[Ca^{2+}] = [HCO_3^-] \quad 6.54$$

Substituting this into 6.53, we obtain:

$$[Ca^{2+}] = P_{CO_2} \frac{K_1 K_{sp-cal} K_{sp-CO_2}}{4 K_2 \gamma_{Ca^{2+}} \gamma_{HCO_3^-}^2 [Ca^{2+}]^2} \quad 6.55$$

or

$$[Ca^{2+}] = \left\{ P_{CO_2} \frac{K_1 K_{sp-cal} K_{sp-CO_2}}{4 K_2 \gamma_{Ca^{2+}} \gamma_{HCO_3^-}^2} \right\}^{1/3} \quad 6.56$$

There are two interesting aspects to this equation. First, the calcium ion concentration, and therefore calcite solubility, increases with increasing P_{CO_2} . This might seem counter-intuitive at first, as one might think that that increasing P_{CO_2} should produce an increase the carbonate ion concentration and therefore drive the reaction toward precipitation. However, increasing P_{CO_2} decreases pH, which de-

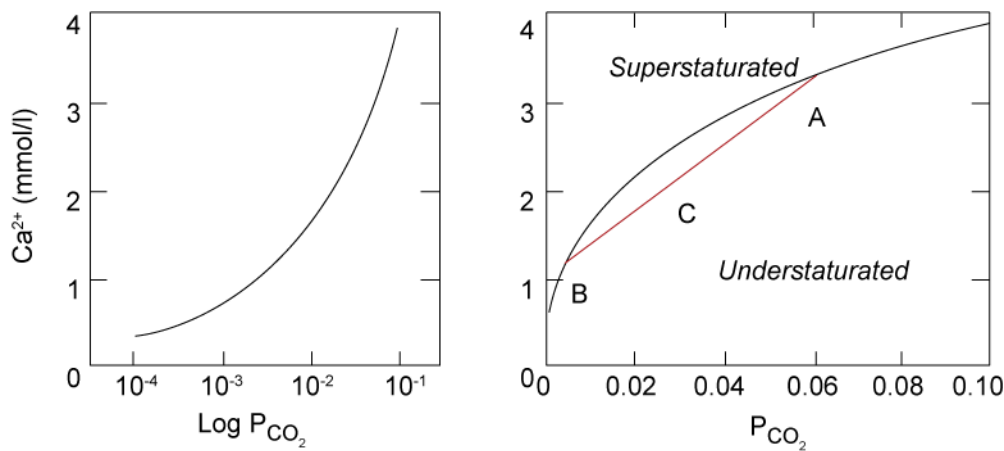


Figure 6.11. Concentration of calcium ion in equilibrium with calcite at 25°C and 1 atm as a function of P_{CO_2} . From Drever (1988).

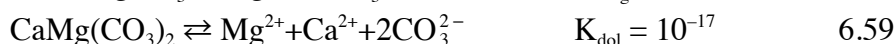
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creases CO_3^{2-} concentration, and therefore drives the reaction towards dissolution. Second, calcium ion concentration varies with the one-third power of P_{CO_2} (Figure 6.11). Because of this non-linearity, mixing of two solutions, both of which are saturated in Ca^{2+} with respect to calcite, can result in the mixture being undersaturated with respect to Ca^{2+} . For example, consider the mixing of stream and ground water. Stream water is in equilibrium with the atmosphere for which P_{CO_2} is $10^{-3.5}$. On the other hand, P_{CO_2} in soils is often as high as 10^{-2} . So mixing between calcite-saturated groundwater and calcite-saturated surface water would produce a solution that is undersaturated with calcite.

Equation 6.56 describes calcite solubility for a system open to exchange with gaseous CO_2 . For a P_{CO_2} of $10^{-3.5}$ (i.e., the atmosphere), this equation yields a calcium concentration of 1.39 mM. Water in pores and fractures in rocks does not exchange with a gas phase. Example 6.8 shows that under those circumstances, less calcite will dissolve; in the case of $P_{\text{CO}_2 \text{ initial}} = 10^{-2}$, calcite saturation is reached at only 0.33 mM, or about a fourth as much. The difference is illustrated in Figure 6.12, which is a plot of $\log [\text{HCO}_3^-]$ vs. pH. Systems in equilibrium with constant P_{CO_2} (open systems) evolve along straight lines on this plot and ultimately reach calcite saturation at higher pH and lower $[\text{HCO}_3^-]$ (and $[\text{Ca}^{2+}]$) than closed systems that initially equilibrate with the same P_{CO_2} . Example 6.9 illustrates the calculation of calcite solubility in a closed system.

6.4.2 Solubility of Mg

There are a number of compounds that can precipitate from Mg-bearing aqueous solutions, including brucite ($\text{Mg}(\text{OH})_2$), magnesite (MgCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), as well as hydrated carbonates such as hydromagnesite ($\text{MgCO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$). The stability of these compounds may be described by the following reactions:



(The solubility of dolomite is poorly known; values for this equilibrium constant vary between $10^{-16.5}$ and 10^{-20} .)

We can use these reactions and their equilibrium constants, together with the reactions for the carbonate system (equ. 6.15-6.17) to construct predominance diagrams for Mg-bearing solutions in equilibrium with these phases. For example, for reaction 6.57, we may derive the following relationship (assuming the solid is pure):

$$\log a_{\text{Mg}^{2+}} = -pK_{\text{bru}} + 2pK_{\text{w}} - 2pH = 16.4 - 2pH \quad 6.60$$

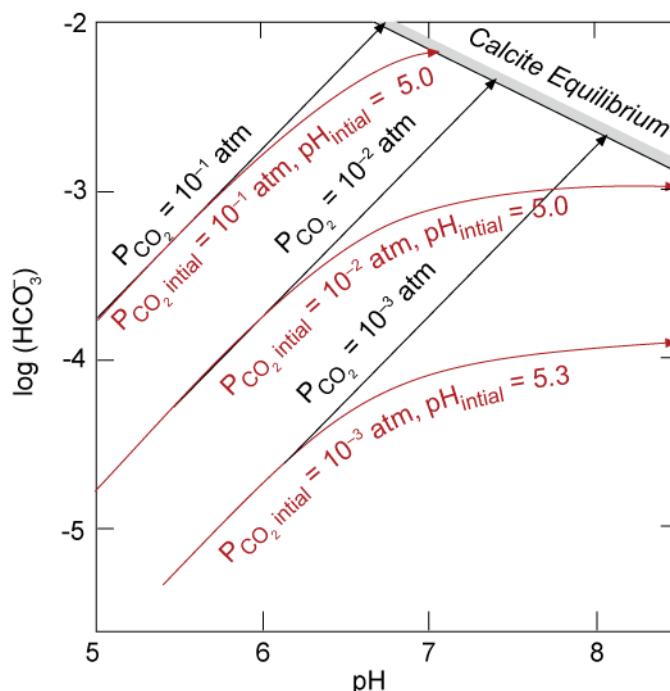


Figure 6.12. Comparison of the evolution of systems with constant P_{CO_2} (open systems) with those closed to gas exchange. After Stumm and Morgan (1996) and Deines et al. (1974).

Example 6.9. Calcite Solubility in a Closed System

Suppose ground water initially equilibrates with a P_{CO_2} of 10^{-2} and thereafter is closed to gas exchange, so that there is a fixed ΣCO_2 initial. The water then equilibrates with calcite until saturation is reached. What will be the final concentration of calcium in the water. Assume ideal behavior and an initial calcium concentration of 0.

Answer: Since the system is closed, a conservation equation is a good place to start. We can write the following conservation equation for total carbonate:

$$\Sigma\text{CO}_2 = \Sigma\text{CO}_2\text{initial} + \Sigma\text{CO}_2\text{from calcite}$$

Since dissolution of one mole of calcite adds one mole of ΣCO_2 for each mole of Ca^{2+} , this equation may be rewritten as:

$$\Sigma\text{CO}_2 = \Sigma\text{CO}_2\text{initial} + [\text{Ca}^{2+}]$$

Neglecting the contribution of the carbonate ion to total carbonate, this equation becomes:

$$[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] = ([\text{H}_2\text{CO}_3]_{\text{initial}}) + [\text{Ca}^{2+}] \quad 6.61$$

where $([\text{H}_2\text{CO}_3]_{\text{initial}})$ denotes that amount of H_2CO_3 calculated from equation 6.21 for equilibrium with CO_2 gas; in this case a partial pressure of 10^{-2} . This can be rearranged to obtain:

$$([\text{H}_2\text{CO}_3]_{\text{initial}}) = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] - [\text{Ca}^{2+}] \quad 6.62$$

Further constraints are provided by the three carbonate equilibrium product expressions (6.21–6.23) as well as the solubility product for calcite (6.50), and the charge balance equation. We assume a final pH less than 9 and no other ions present, so the charge balance equation reduces to equation 6.54. From equation 6.18 and the value of K_{CO_2} in Table 6.1, $[\text{H}_2\text{CO}_3]_{\text{initial}} = 10^{-2} \times 10^{-1.47}$ M. Dividing equation 6.19 by 6.20 yields:

$$\frac{K_1}{K_2} = \frac{[\text{HCO}_3^-]^2}{[\text{H}_2\text{CO}_3][\text{CO}_3^{2-}]}$$

Then substituting equations 6.52, 6.54, and 6.62 gives:

$$\frac{K_1}{K_2} = \frac{4[\text{Ca}^{2+}]^3}{K_{\text{sp-cal}} \{[\text{H}_2\text{CO}_3]_{\text{initial}} - [\text{Ca}^{2+}]\}}$$

Into this equation we substitute $P_{\text{CO}_2} K_{\text{CO}_2} = [\text{H}_2\text{CO}_3]$ and rearrange to obtain:

$$[\text{Ca}^{2+}]^3 + \frac{K_1 K_{\text{cal}}}{4K_2} [\text{Ca}^{2+}] - \frac{K_1 K_{\text{cal}} K_{\text{CO}_2}}{4K_2} (P_{\text{CO}_2\text{initial}}) = 0 \quad 6.63$$

This is a cubic equation that is readily solved for $[\text{Ca}^{2+}]$. For an initial P_{CO_2} of 10^{-2} , we calculate a calcium concentration of 0.334 mM.

where we use the notation $pK = -\log(K)$. For reaction 6.58, the equilibrium constant relationship may be written as:

$$\log \frac{a_{\text{Mg}^{2+}}}{a_{\text{MgCO}_3(\text{s})}} = -\log a_{\text{CO}_3^{2-}} - pK_{\text{mag}} \quad 6.64$$

However, the carbonate concentration will depend on both total carbonate (or the partial pressure of CO_2) and pH. To simplify things, let's specify that the solid is pure, the solution ideal, and $\Sigma\text{CO}_2 = 10^{-2.5}$ M. Then we can think of three limiting cases: where carbonic acid, bicarbonate ion, and carbonate ion predominate. In the latter case, $[\text{CO}_3^{2-}] \approx \Sigma\text{CO}_2 = 10^{-2.5}$ M, so we have:

$$\log[\text{Mg}^{2+}]_{\text{aq}} = 2.5 - pK_{\text{mag}} = -5.0 \quad 6.64a$$

When bicarbonate ion predominates, $[\text{HCO}_3^-] \approx \Sigma\text{CO}_2 = 10^{-2.5}$ M, and the carbonate ion concentration is:

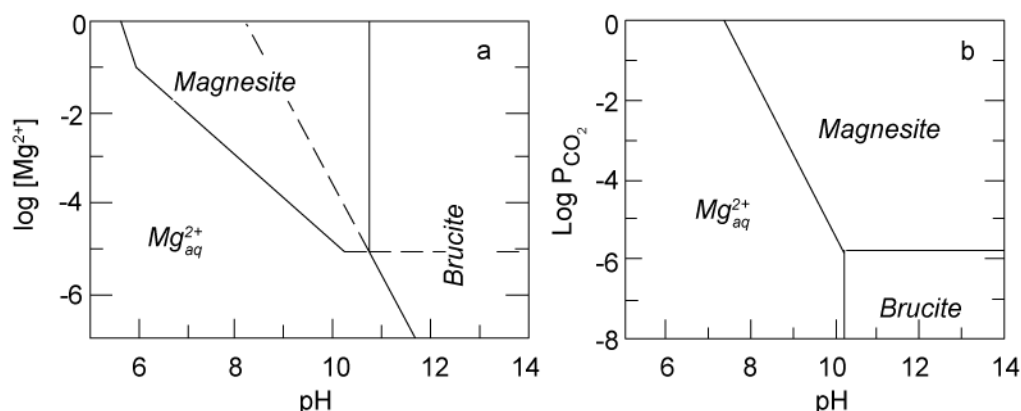


Figure 6.13. Predominance diagrams for Mg-bearing phases in equilibrium with aqueous solution. Total CO₂ is fixed at 10^{-2.5} M in 6.14a. The concentration of Mg²⁺ is fixed at 10⁻⁴ M in 6.14b. After Stumm and Morgan (1996).

$$\log[\text{CO}_3^{2-}] = -pK_2 + \log[\text{HCO}_3^-] + pH = -12.88 + pH$$

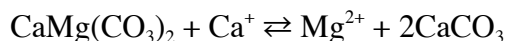
Substituting this into 6.64 we have: $\log[\text{Mg}^{2+}] = 5.33 - pH$ 6.64b

Finally, when carbonic acid predominates, [H₂CO₃] ≈ ΣCO₂ = 10^{-2.5} M. The carbonate ion concentration as a function of [H₂CO₃] is given by equation 6.39b. Taking the log and substituting into equation 6.64, we have:

$$\log[\text{Mg}_{aq}^{2+}] = -pK_{mag} + pK_1 + pK_2 - \log[\text{H}_2\text{CO}_3] - 2pH = 26.68 - 2pH$$
 6.64c

We can use these equations to construct *stability, or predominance diagrams* in a manner similar to that used to construct pe-pH predominance diagrams (Chapter 3). Equations 6.63-6.64c express the Mg ion concentration as a function of pH and hence represent lines on a plot of log [Mg²⁺] vs. pH. The lines divide the diagram (Figure 6.13) into 3 regions: (1) where only an Mg-bearing aqueous solution is stable (2) where magnesite is stable and (3) where brucite is stable. For example, on a plot of log[Mg²⁺] vs. pH, the predominance boundary between Mg²⁺_{aq} and brucite plots as a line with a slope of -2 and an intercept of +16.4. Figure 6.13b shows a predominance diagram for this system, but where the Mg²⁺ concentration is fixed and P_{CO₂} and pH are the variables.

Virtually all natural solutions will contain dissolved calcium as well as magnesium. This being the case, we must also consider the stability of dolomite. We can construct similar predominance diagrams for these systems but we must add an additional variable, namely the Ca²⁺ concentration. To describe the relative stability of dolomite and calcite, it is more convenient to express the solubility of dolomite as:



because the reaction contains calcite as well as dolomite. Since this reaction can be constructed by subtracting 2 times the calcite dissolution (equ. 6.27) from the dolomite dissolution (6.59), the equilibrium constant for this reaction can be calculated from:

$$K = \frac{K_{dol}}{K_{cal}^2}$$

Figure 6.14 illustrates the stability of magnesite, dolomite, brucite and calcite as a function of P_{CO₂} and the Ca²⁺/Mg²⁺ concentration ratio. Whether any of these phases are stable

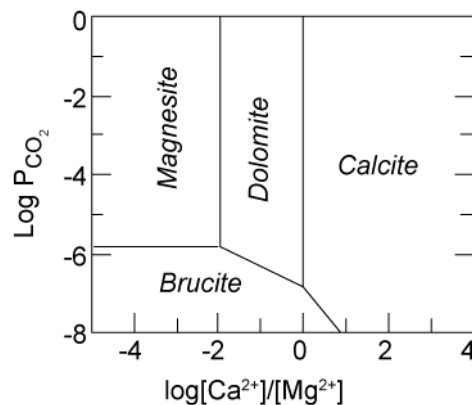
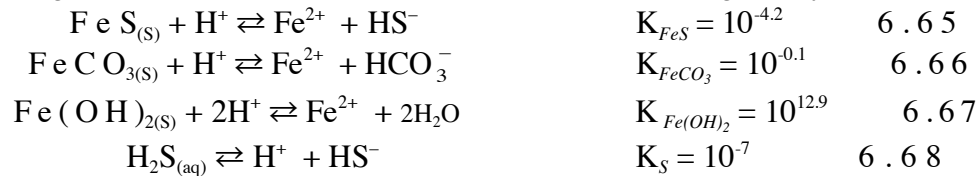


Figure 6.14. Stability of magnesite, dolomite, calcite, and brucite in equilibrium with a Mg- and Ca-bearing aqueous solution.

relative to a Mg^{2+} -bearing solution depends on the Mg^{2+} concentration, which is not specified in the graph.

EXAMPLE 6.10. CONSTRUCTING STABILITY DIAGRAMS

Using the equilibrium constant data below as well as from Table 6.1, construct a stability diagram showing the stability of FeS, siderite ($FeCO_{3(s)}$), and $Fe(OH)_2$ as a function of total sulfide concentration and pH assuming $\Sigma CO_2 = 5 \times 10^{-2} M$, $Fe^{2+} = 10^{-6} M$, and ideal behavior. Neglect any S^{2-} .



Answer: Let's first consider reaction 6.65 above. Our first step is to set up an equation that describes the concentration of HS^- as a function of pH. From the conservation of sulfur, we have:

$$\Sigma S = [H_2S] + [HS^-]$$

From the equilibrium constant expression for the dissociation of H_2S , we may substitute:

$$[H_2S] = \frac{[H^+][HS^-]}{K_S} \text{ and obtain: } \Sigma S = \frac{[H^+][HS^-]}{K_S} + [HS^-] \quad 6.69$$

Solving for $[HS^-]$ we have: $[HS^-] = \Sigma S \frac{K_S}{K_S + [H^+]}$

We substitute this into the FeS (pyrrhotite) solubility product and solving for ΣS we have:

$$\Sigma S = \frac{K_{FeS}[H^+](K_S + [H^+])}{[Fe^{2+}]K_S}$$

or in log form: $\log(\Sigma S) = \log(K_S + 10^{-pH}) - pH - \log([Fe^{2+}]) - pK_{FeS} + pK_S \quad 6.70$

This plots as line ① on our ΣS vs. pH stability diagram (Figure 6.15). The area above the line is the region where FeS is stable.

Next, let's consider reaction 6.66, the solubility of siderite. We need an equation describing the concentration of HCO_3^- as a function of pH and ΣCO_2 , which is equation 6.29. Substituting this into the siderite solubility product we have:

$$K_{FeCO_3} = \frac{[Fe^{2+}]\Sigma CO_2}{\left\{ \frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]} \right\} [H^+]}$$

or in log form:

$$pH + \log[Fe^{2+}] + \log[\Sigma CO_2] - \log\left\{ \frac{10^{-pH}}{K_1} + 1 + \frac{K_2}{10^{-pH}} \right\} + pK_{FeCO_3} = 0 \quad 6.71$$

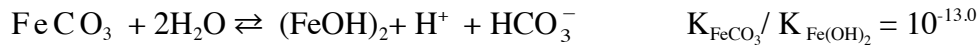
An approximate solution may be found by assuming $HCO_3^- = \Sigma CO_2$, which yields $pH = 7.20$. An exact solution requires an indirect method. Using the Solver in Microsoft Excel™, we obtain $pH = 7.25$, very close to our approximate solution (Solver uses a succession of "intelligent" guesses to find solutions to equations, such as 6.71 that have no direct solution). Thus siderite will precipitate when the pH is greater than 8.21 and, not surprisingly, this is independent of ΣS . The boundary between the Fe^{2+} and $FeCO_3$ field is then a vertical line (line ②) at $pH = 7.25$.

Now let's consider the solubility of ferrous iron hydroxide, The condition for precipitation of $Fe(OH)_2$ is described by the equation:

$$pH = \frac{pK_{Fe(OH)_2} - \log[Fe^{2+}]}{2} = 9.45 \quad 6.72$$

Thus Fe(OH)₂ will not precipitate until pH reaches 9.5, i.e., above the point where FeCO₃ precipitates, so there is no boundary between a Fe(OH)₂ phase and a Fe²⁺-bearing solution.

Next we need equations that describe the reactions between solid phases. A reaction between FeCO₃ and Fe(OH)₂ can be obtained by subtracting reaction 6.67 from reaction 6.66. The corresponding equilibrium constant is obtained by dividing 6.67 by 6.66:



From this we derive: $pH = \log [\text{HCO}_3^-] + 13.0$ 6.73

We can obtain an approximate solution, by simply assuming all carbonate is bicarbonate, in which case, we obtain pH = 11.69. Or we can substitute equation 6.29 for HCO₃⁻ and use the Solver in Excel™, which yields an exact solution of pH = 11.02. Not surprisingly, our approximate solution is less accurate than in the previous case because at this high pH, the carbonate ion makes up a significant fraction of the total carbonate (Figure 6.1). The boundary between the FeCO₃ and Fe(OH)₂ fields is thus a vertical line at pH = 10.02 (line ③).

The boundary between FeS and FeCO₃ is found by subtracting reaction 6.66 from 6.65 and dividing the corresponding equilibrium constants:



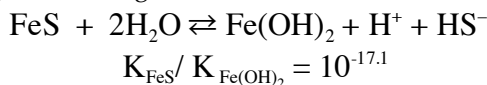
Substituting 6.68 and 6.29 into the corresponding equilibrium constant expression, we have:

$$\begin{aligned} -pK_{\text{pyr-sid}} &= \log[\text{HS}^-] - \log[\text{HCO}_3^-] \\ &= \log \Sigma S - pK_s - \log(K_s + [\text{H}^+]) \\ &\quad - \log \Sigma \text{CO}_2 + \log \left\{ \frac{[\text{H}^+]}{K_1} + 1 + \frac{K_2}{[\text{H}^+]} \right\} \end{aligned}$$

Solving for ΣS and substituting 10^{-pH} for [H⁺], we have:

$$\begin{aligned} \log \Sigma S &= -pK_{\text{pyr-sid}} + pK_s + \log(K_s + 10^{-pH}) \\ &\quad + \log \Sigma \text{CO}_2 - \log \left\{ \frac{10^{-pH}}{K_1} + 1 + \frac{K_2}{10^{-pH}} \right\} \end{aligned}$$

This plots as line ④ on our diagram. Finally, the reaction between FeS and Fe(OH)₂ is obtained by subtracting reaction 6.67 from reaction 6.65:



From the equilibrium constant equation we obtain an expression of ΣS as a function of pH:

$$\log \Sigma S = pH - pK_{\text{FeS-Fe(OH)}_2} + pK_s + \log(K_s + 10^{-pH})$$

This plots as line ⑤ on our diagram, which is now complete.

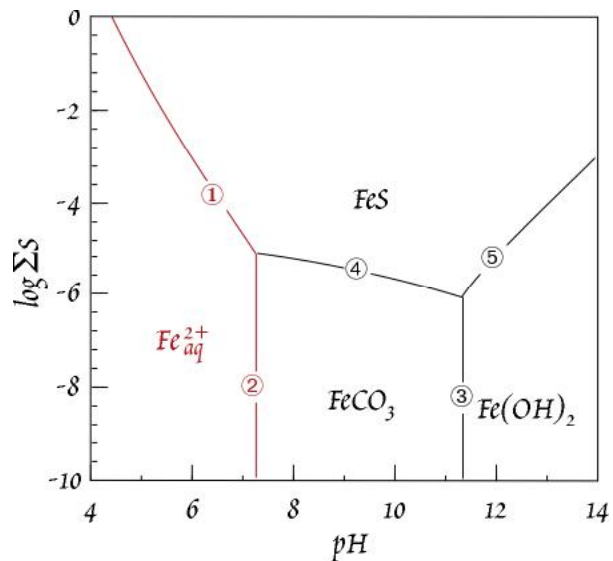
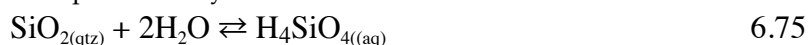


Figure 6.15. Stability diagram showing the stable solid Fe-bearing phases in equilibrium with a solution containing 10⁻⁶ M Fe²⁺ and 5 × 10⁻³ M ΣCO₂.

6.4.3 Solubility of SiO₂

Silicon is the most common element on the Earth's surface after oxygen. Its concentration in solution plays an important role in determining how weathering will proceed.

The dissolution of silica may be represented by the reaction:



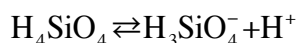
The equilibrium constant expression is simply:

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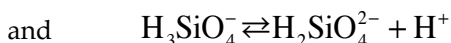
$$K_{qtz} = a_{H_4SiO_4} = 10^{-4} \text{ at } 25^\circ\text{C} \quad 6.76$$

This is to say, water is saturated with respect to quartz when the concentration of H_2SiO_4 is 10^{-4} moles per kilogram, or about 7.8 ppm by weight SiO_2 .

However, there are some complicating factors. First, precipitation of quartz seems to be strongly kinetically inhibited. Equilibrium is more likely to be achieved with amorphous silica, the equilibrium constant for which is 2×10^{-3} (~115 ppm). Second, H_4SiO_4 is a weak acid and undergoes successive dissociation with increasing pH:



$$K_1 = \frac{a_{H_3SiO_4^-} a_{H^+}}{a_{H_4SiO_4}} = 10^{-9.9}$$



$$K_2 = \frac{a_{H_2SiO_4^{2-}} a_{H^+}}{a_{H_3SiO_4^-}} = 10^{-11.7}$$

The total dissolved silica concentration will be the sum of H_4SiO_4 , $H_3SiO_4^-$, and $H_2SiO_4^{2-}$. Assuming activity coefficients of unity, the concentration of dissolved silica is then:

$$[SiO_2]_T = [H_4SiO_4] \left\{ 1 + \frac{K_1}{a_{H^+}} + \frac{K_1 K_2}{a_{H^+}^2} \right\} \quad 6.77$$

From equation 6.77, we would expect silica solubility to be pH dependent. This dependence is illustrated in Figure 6.16.

We could have defined the second dissociation reaction as:



In which case, the equilibrium constant would be:

$$K_2^* = \frac{a_{H_2SiO_4^{2-}} a_{H^+}^2}{a_{H_4SiO_4}} = 10^{-9.9} \times 10^{-11.7} = 10^{-21.6}$$

and equation 6.67 would have been:

$$[SiO_2]_T = [H_4SiO_4] \left\{ 1 + \frac{K_1}{a_{H^+}} + \frac{K_2^*}{a_{H^+}^2} \right\} \quad 6.77a$$

The concentration of SiO_{2T} we calculate in this way would, of course, be identical. The point is, reactions and their corresponding equilibrium constants can be expressed in various ways, and we need to be alert to this.

6.4.4 Solubility of $Al(OH)_3$ and Other Hydroxides

The hydroxide is the least soluble salt of many metals. Therefore, it is the solubility of their hydroxides that controls the solubility of these metals in natural waters. These are shown in Figure 6.17. Since these dissolution reactions involve OH^- , they are pH dependent, and the slope of the solubility curve depends on the valence of the metal (e.g., -3 for Fe^{3+} , -2 for Fe^{2+} , -1 for Ag^+). Let's consider in more detail the solubility of gibbsite, the hydroxide of aluminum.

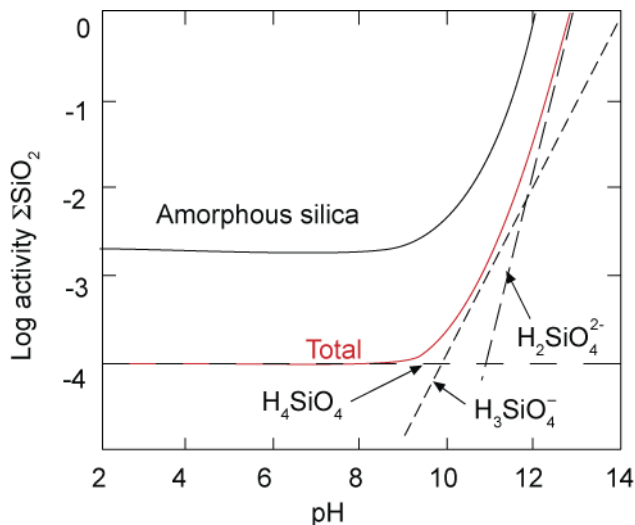


Figure 6.16. Log activity of dissolved silica in equilibrium with quartz and amorphous silica (dashed line) as a function of pH. After Drever (1988).

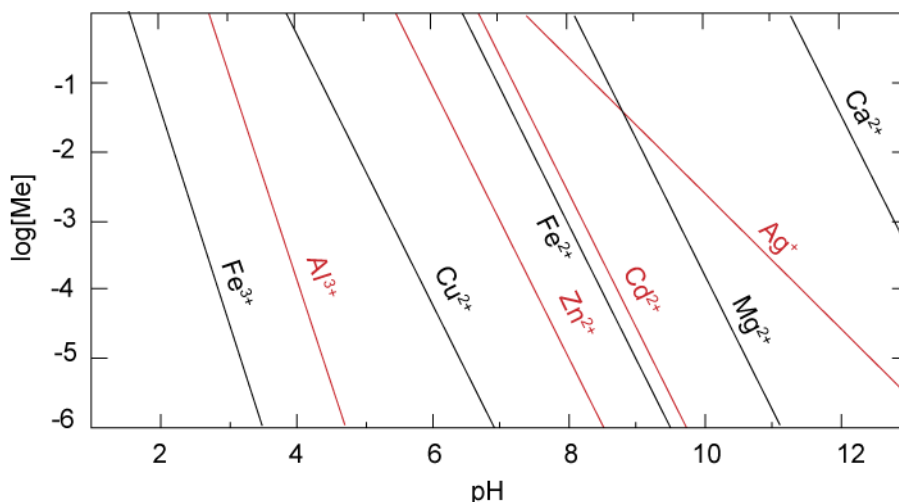
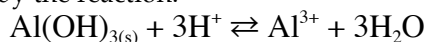


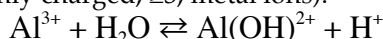
Figure 6.17. Solubility of metal hydroxides as a function of pH. After Stumm and Morgan (1981).

Dissolution of gibbsite ($\text{Al}(\text{OH})_3$) can be described by the reaction:

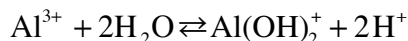


$$K_{gib} = \frac{a_{\text{Al}^{3+}}}{a_{\text{H}^+}^3} = 10^{-8.1} \quad 6.78$$

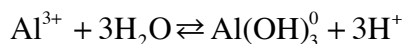
However, a complication arises from hydrolyzation of the aluminum, which occurs in solutions that are not highly acidic (hydrolyzation is typical of many of the highly charged, ≥ 3 , metal ions):



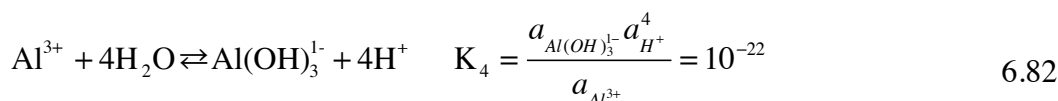
$$K_1 = \frac{a_{\text{Al}(\text{OH})^{2+}} a_{\text{H}^+}}{a_{\text{Al}^{3+}}} = 10^{-5} \quad 6.79$$



$$K_2 = \frac{a_{\text{Al}(\text{OH})_2^+} a_{\text{H}^+}^2}{a_{\text{Al}^{3+}}} = 10^{-9.3} \quad 6.80$$



$$K_3 = \frac{a_{\text{Al}(\text{OH})_3^0} a_{\text{H}^+}^3}{a_{\text{Al}^{3+}}} = 10^{-16} \quad 6.81$$



The total dissolved aluminum activity is given by:

$$a_{\text{Al}^{3+}T} = a_{\text{Al}^{3+}} \left\{ 1 + \frac{K_1}{a_{\text{H}^+}} + \frac{K_2}{a_{\text{H}^+}^2} + \frac{K_3}{a_{\text{H}^+}^3} + \frac{K_4}{a_{\text{H}^+}^4} \right\} \quad 6.83$$

Figure 6.18 shows the activities of the various aluminum species and total aluminum as a function of pH. The solubility of Al is low except at low and high pH, and that as pH increases Al^{3+} becomes increasingly hydrolyzed. Also note that where positively charged species dominate, e.g., Al^{3+} , solubility

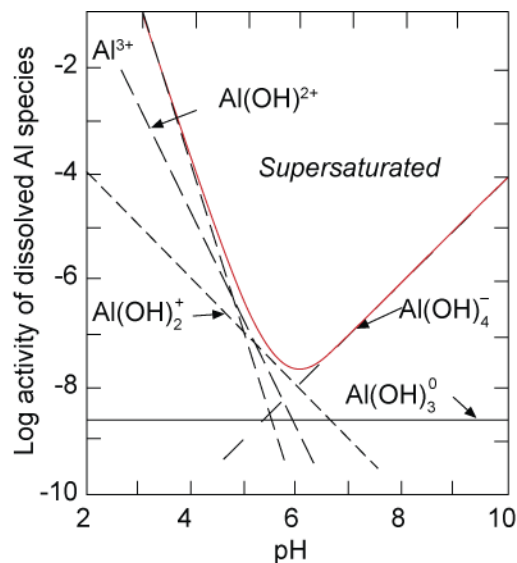


Figure 6.18. Log activity of dissolved aluminum species and total Al (solid red line) in equilibrium with gibbsite as a function of pH.

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increases with decreasing pH; where negatively charged species dominate, solubility increases with increasing pH. Minimum solubility occurs in the range of pH of natural waters (which is just as well because it has some toxicity).

Equation 6.83 is a general result that can be applied to other metals that undergo hydrolyzation reactions, *when the reactions are expressed in the same form as those above*. A general form of this equation would thus be:

$$[M]_T = [M^z] \left\{ 1 + \frac{K_1}{a_{H^+}} + \frac{K_2}{a_{H^+}^2} + \frac{K_3}{a_{H^+}^3} + \dots \right\} \quad 6.84$$

Thus iron and other metals show a pH dependence similar to Al. For Fe, the relevant equilibrium constants are:



Using these equilibrium constants, the solubility of amorphous goethite as a function of pH is readily calculated and is shown in Figure 6.19.

6.4.5 Dissolution of Silicates and Related Minerals

The concentrations of Al and Si will usually not be controlled by equilibrium with quartz and gibbsite, rather by equilibrium with other silicates. An example of this is shown in Figure 6.20, which shows the concentration of dissolved Al in equilibrium with gibbsite, kaolinite and pyrophyllite at four different activities of dissolved silica. Only at the lowest dissolved silica concentrations will gibbsite precipitate before one of the aluminosilicates.

For the most part, silicates do not dissolve in the conventional sense, rather they react with water to release some ions to solution and form new minerals in place of the original ones. This phenomenon is known as *incongruent solution*. In considering such reactions, we can usually assume all Al remains in the solid phase. If we consider only Al and Si, a simple reaction might be the breakdown of kaolinite to form gibbsite plus dissolved silica:



Assuming the solid phases are pure, the equilibrium constant for this reaction is simply:

$$K = a_{\text{H}_4\text{SiO}_4} = 10^{-4.4} \quad 6.87$$

which tells us that at H_4SiO_4 activities greater than $10^{-4.4}$, kaolinite is more stable than gibbsite. Similar reactions can, of course, be written between other phases, such as kaolinite and pyrophyllite. Introducing other ions into the system allows the possibility of other phases and other reactions, e.g.:

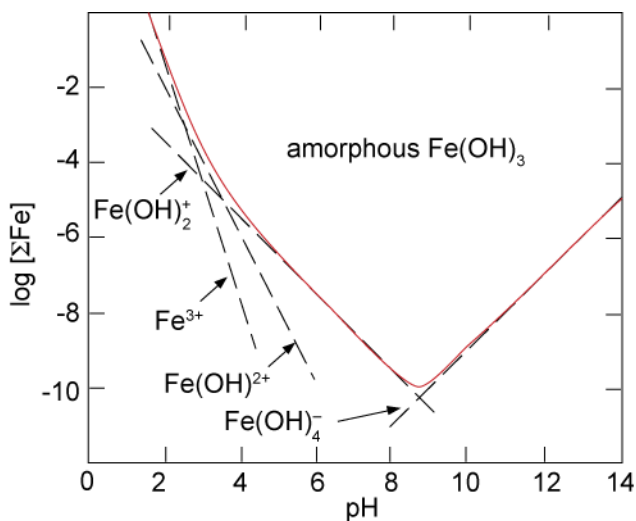
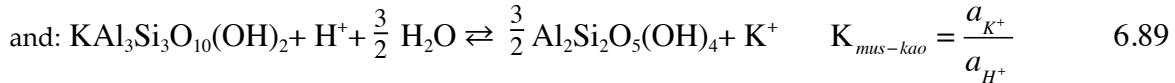
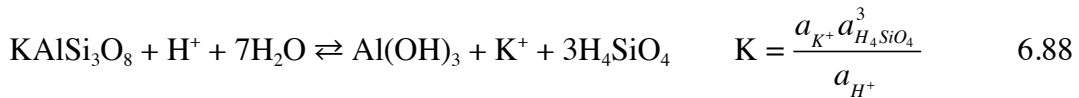
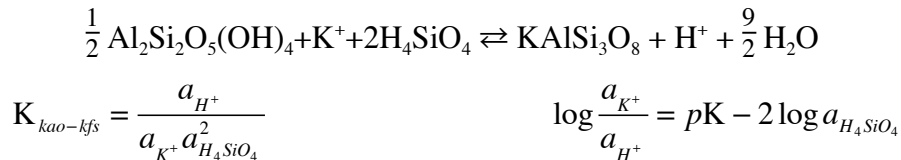


Figure 6.19. Solubility of goethite as a function of pH. Solubility of individual Fe-hydroxide species shown as dashed lines.



From a series of such reactions and their corresponding equilibrium constant expressions, we can construct stability diagrams such as the one in Figure 6.21. The procedure for constructing this and similar diagrams is essentially similar to that used in construction of pe-pH diagrams and is illustrated in Example 6.10. In the case of Figure 6.21, we seek an equilibrium constant expression containing the $a_{\text{K}^+}/a_{\text{H}^+}$ ratio and the activity of H_4SiO_4 . From this expression we determine the slope and intercept, which allows us to plot the predominance boundary. For example, the boundary between the kaolinite and muscovite fields is given by equation 6.89. The equilibrium constant for the reaction is 10^4 , so the boundary is a line with slope 0 at $\log a_{\text{K}^+}/a_{\text{H}^+} = 4$. The boundary between gibbsite and kaolinite is reaction 6.86, and equation 6.87, written in log form, defines the line dividing the two regions. This boundary thus plots as a vertical line at $\log a_{\text{H}_4\text{SiO}_4} = -4.4$. The kaolinite - K-feldspar boundary is the reaction:



The boundary thus plots as a line with a slope of -2 and an intercept equal to the negative of the log of the equilibrium constant. Boundaries for the remaining fields can be derived similarly.

The fields in Figure 6.21 show the phase that is the most stable of those we considered in constructing

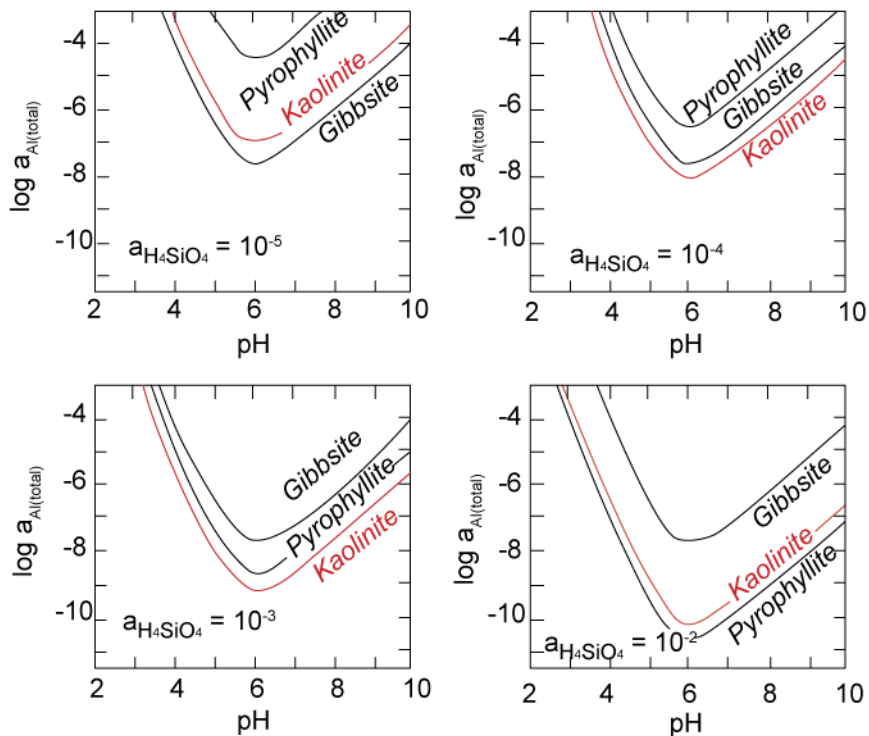


Figure 6.20. Total dissolved Al activity in equilibrium with gibbsite, pyrophyllite, and kaolinite as a function of pH at different dissolved silica activities. After Drever (1988).

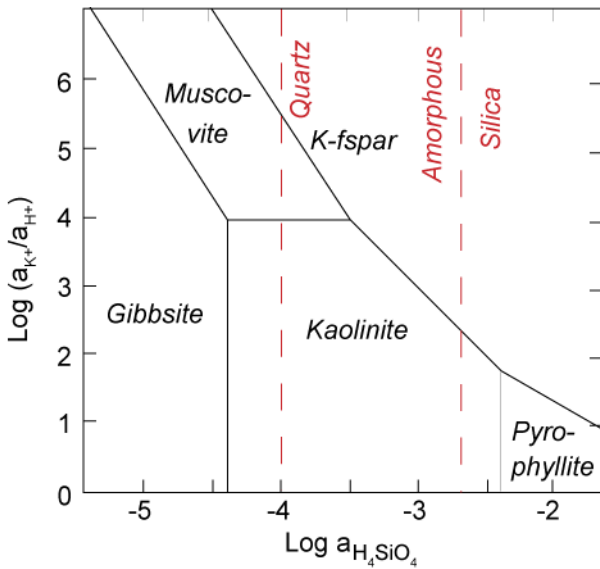


Figure 6.21. Stability diagram for the system $K_2O-Al_2O_3-SiO_2-H_2O$ at $25^\circ C$. After Drever (1988).

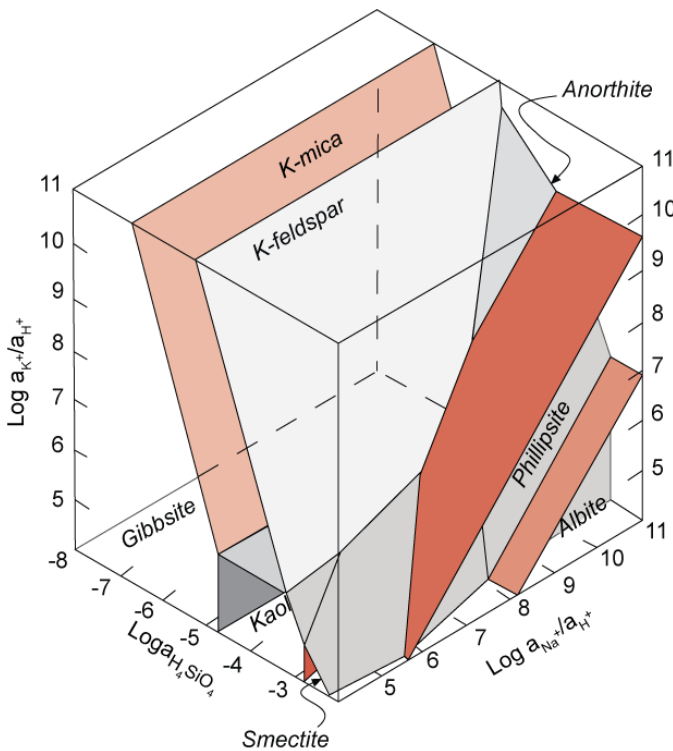


Figure 6.22. Stability diagram for the system $K_2O-Na_2O-CaO-Al_2O_3-SiO_2-H_2O$ at $25^\circ C$. After Garrels and Christ (1965).

the diagram. (Strictly speaking, it does not tell us whether the phase can be expected to precipitate or not, as this depends on the Al activity; however, because of the low solubility of Al, an aluminum-bearing phase can be expected to be stable in most instances.) By considering sodium and calcium as well as potassium, we can construct a 3-dimensional stability diagram, such as that in Figure 6.22, in a similar manner.

Because many low-temperature reactions involving silicates are so sluggish, equilibrium constants are generally calculated from thermodynamic data rather than measured.

6.5 CLAYS AND THEIR PROPERTIES

Clays are ubiquitous on the surface of the Earth. Unfortunately, the term *clay* has two meanings in geology: in a mineralogical sense it refers to a group of sheet silicates, in another sense it refers to the finest fraction of a sediment or soil. In addition to clay minerals, fine-grained oxides and hydroxides are present in the 'clay fraction'. Clays, in both senses, exert important controls on the composition of aqueous fluids, both because of chemical reactions that form them and because of their sorptive and ion exchange capacities. Generally, only clays in the mineralogical sense have true ion-exchange capacity, where ions in the clay can be exchanged for ions in the surrounding solution, but oxides and hydroxides can adsorb and desorb ions on their surfaces. We will first consider the mineralogy of the true clays, then consider their interaction with solution.

6.5.1 Clay Mineralogy

Clay minerals (*sensu stricto*) are sheet silicates. We can think of each sheet in a clay mineral as consisting of layers of silica tetrahedra bound to a hydroxide layer in which the cation (most commonly Al, Mg, or Fe) is in octahedral coordination much as in pure hydroxide minerals such as gibbsite ($Al(OH)_3$) or brucite ($Mg(OH)_2$). Brucite and gibbsite are structurally similar to

each other except that in gibbsite every third octahedral site is left empty to maintain charge balance. This is illustrated in Figure 6.23. Because only 2 out of 3 octahedral sites are occupied, gibbsite is said

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to have a *dioctahedral* structure, while brucite is said to be *trioctahedral*. This terminology also applies in clay minerals in exactly the same sense.

6.5.1.1 Kaolinite Group (1:1 Clays)

The simplest clays consist of a tetrahedral silicate layer and an octahedral hydroxide layer, hence the term 1:1 clays. Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, is a good example. The structure of kaolinite is shown in Figure 6.24. Its unit cell consists of a layer of silica tetrahedra bound to an octahedral alumina layer whose structure is very similar to that of gibbsite except that some hydroxyls are replaced by oxygens. Note that individual sheets are not bound together; they are held together only by van der Waals interactions, which are quite weak. The structure of serpentine, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, is similar to that of kaolinite, with Mg replacing Al, and every octahedral site is occupied. In both minerals, a mismatch in the spacing of octahedra and tetrahedra results

in a curvature of the lattice. Also successive layers of kaolinite are generally stacked in a random manner.

6.5.1.2 Pyrophyllite Group (2:1 Clays)

This is a large group of clay minerals consisting of a "hydroxide layer" sandwiched between two layers of silica tetrahedra, hence the term 2:1 clays. More of the hydroxyls in the hydroxide layer are replaced by oxygen than in 1:1 clays. The simplest two such clays are pyrophyllite, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, and talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. In pyrophyllite, every third octahedral site is vacant, so that it, like kaolinite, is said to be dioctahedral, while serpentine and talc are trioctahedral. The structure of pyrophyllite is shown in Figure 6.25. Other, more complex clays, including those of the smectite group, the bi-

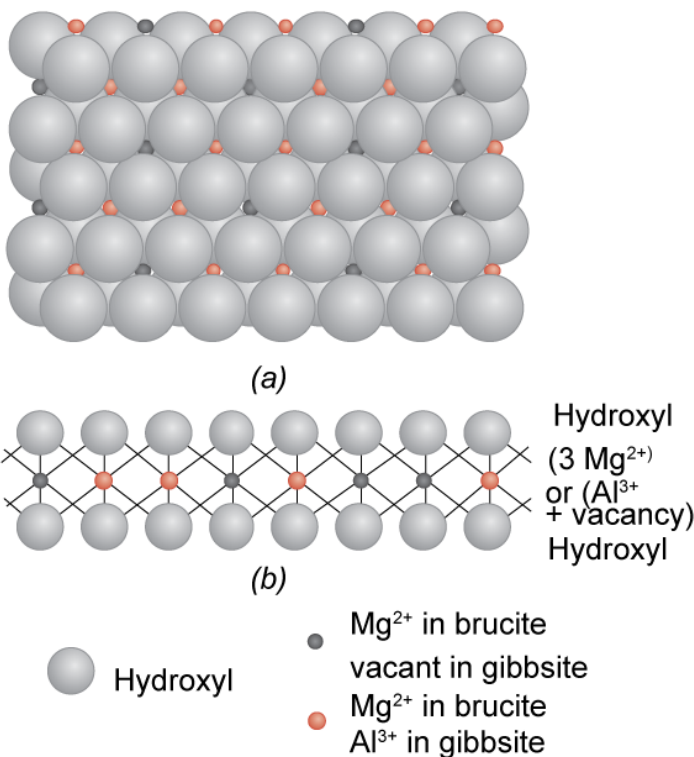


Figure 6.23. Structure of gibbsite and brucite. (a) plan (vertical) view; (b) expanded x-sectional view.

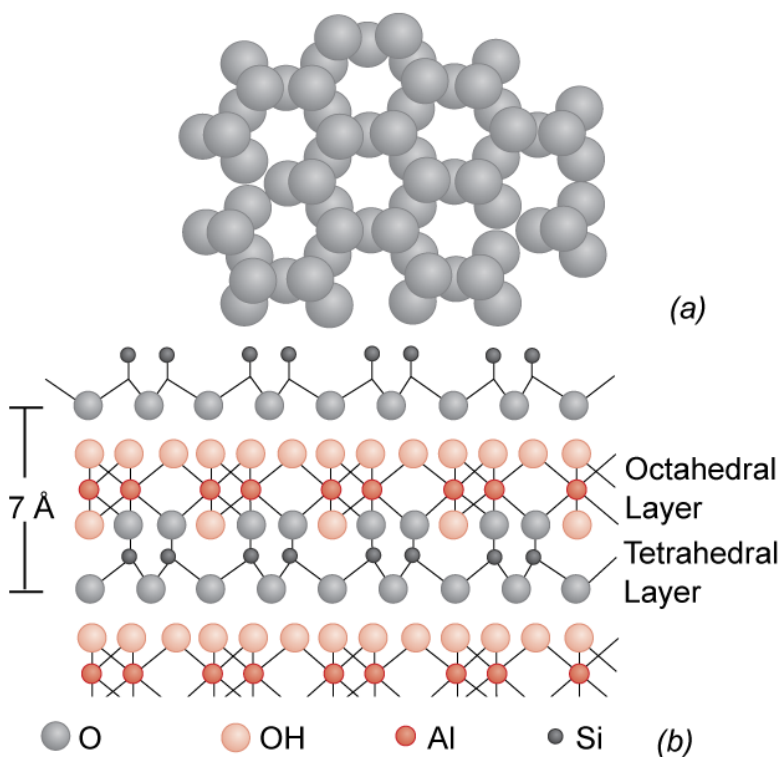


Figure 6.24. Structure of kaolinite. (a) Plan view of the tetrahedral layer. (b) Cross-sectional view.

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otite group, the vermiculite group, saponite, and muscovite, have structures similar to those of pyrophyllite and talc. These are derived in the following ways:

1. Substitution of Al^{3+} for Si^{4+} in the tetrahedral sites resulting in a charge deficiency that is balanced by the presence of a cation between the layers (interlayer positions). When the number of interlayer cations is small, they are generally exchangeable; when the number is large, K is typically the cation and it is not very exchangeable.
2. Substitution of Mg^{2+} , Fe^{2+} , Fe^{3+} or a similar cation for Al^{3+} or substitution of Fe^{2+} , Fe^{3+} , or Al^{3+} for Mg^{2+} in the octahedral layer. Where charge deficiency results, it is balanced by the presence of exchangeable cations in the interlayer sites, or by vacancies in the octahedral sites.

Smectites are distinguished by their expansion to a unit cell thickness of 14 Å upon treatment with ethylene glycol. This expansion results from entry of the ethylene glycol molecule into the interlayer position of the clays. Smectites generally also have water present in the interlayer space, the amount of water being determined by the cation present. Generally there is little water present when the interlayer cation is divalent Mg or Ca, but can be very considerable when the cation is Na. The amount of water also depends on the humidity; as a result smectites, and sodium bearing ones in particular will swell on contact with water, affecting permeability. The most common smectite is montmorillonite, $X_{1/3}(Mg_{1/3}Al_{5/3})Si_4O_{10}(OH)_2 \cdot nH_2O$. The interlayer cation of smectites is

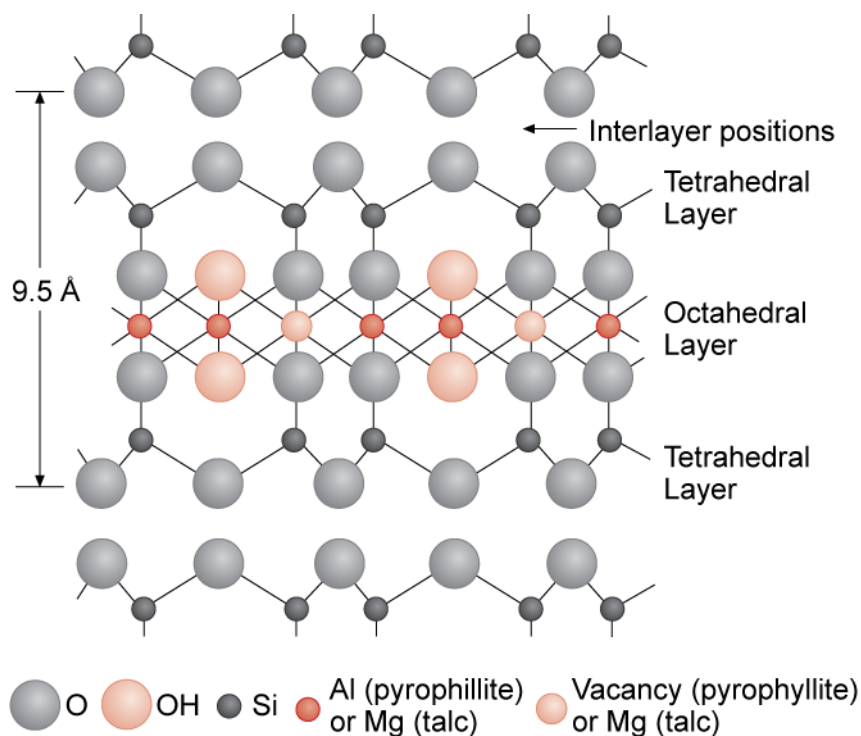


Figure 6.25. Structure of pyrophyllite.

Muscovite (Illite)

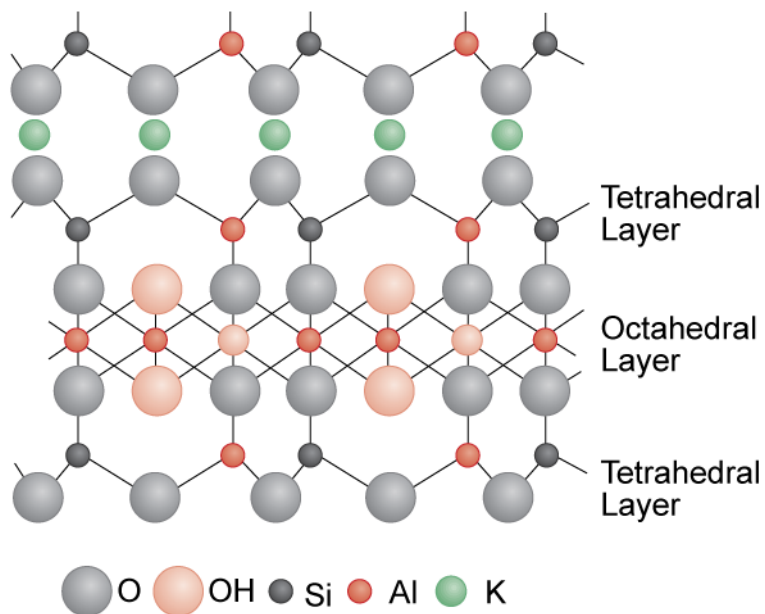


Figure 6.26. Structure of muscovite ($KAl_3Si_3O_{10}(OH)_2$). The structure of the clay illite is similar, but illite typically has less K and Al and more Si than muscovite.

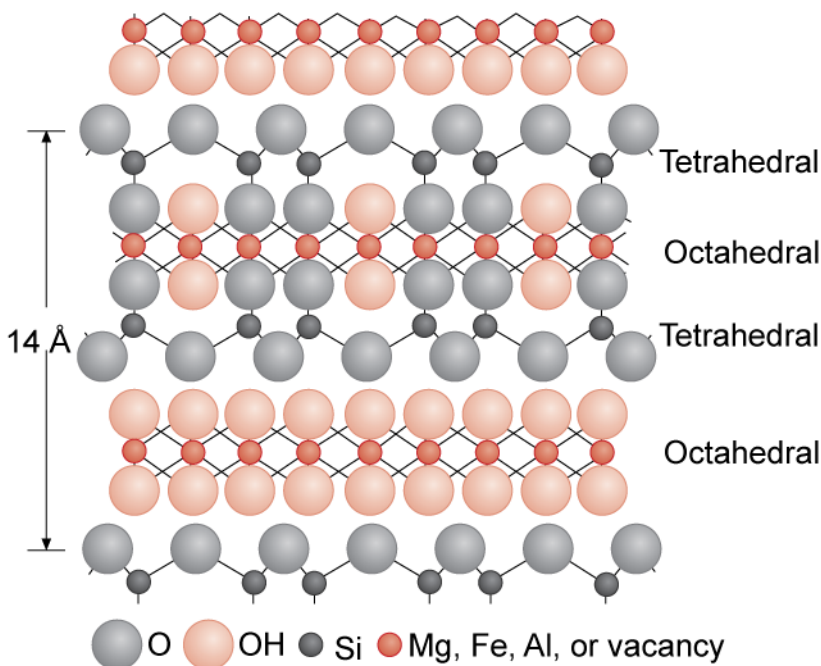


Figure 6.27. Structure of Chlorite.

relatively strongly bound to the interlayer K, which is not normally exchangeable. *Illite* is a name applied to clay-sized micas, though it is sometimes restricted to the dioctahedral mica (muscovite). Generally, illite has less K and Al and more Si than igneous or metamorphic muscovite; in this sense it can be viewed as a solid solution of muscovite and pyrophyllite.

Because of the structural similarity of various 2:1 clays, they can form crystals that consist of layers of more than one type, for example illite-smectite. In addition, layers of gibbsite or brucite may occur in smectite. Different layers may be distributed randomly or may be ordered. These are called, for example, mixed-layer chlorite-smectite or hydroxy-interlayer smectite.

6.5.1.3 Chlorite Group (2:2 clays)

This group is characterized by having a unit cell consisting of two tetrahedral layers and two (hydroxide) octahedral layers. The ideal formula of chlorite is $(\text{Mg,Fe,Al})_6(\text{SiAl})_4\text{O}_{10}(\text{OH})_8$, where the elements in parentheses can be in any proportions. The structure of chlorite is shown in Figure 6.27. Chlorites with unit cells consisting of a single tetrahedral and single octahedral layer also occur and are called septechlorite (because they have a 7 Å spacing; true chlorites have 14 Å spacing), but are less stable and uncommon.

6.5.2 Ion-Exchange Properties of Clays

One of the most important properties of clays is their capacity for ion exchange. In soil science, the term *ion exchange* refers specifically to replacement of an ion adsorbed to the surface by one in solution. However, we shall use the term in a more general sense here, and include as well exchange reactions between ions in solution and ions bound within the solid. The ability of a substance to exchange ions is called the *ion exchange capacity* and is generally measured in equivalents or milliequivalents (meq). Ion exchange capacities of clays are listed in Table 6.03.

The exchange reaction of two monovalent ions between clay and solution may be written:

exchangeable: in a NaCl solution it will be Na, in a CaCl_2 solution it will be Ca, etc.

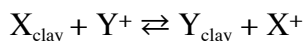
Vermiculites have a higher net charge on the 2:1 layer (that is, there is greater cation deficiency). As a result, the electrostatic forces holding the layers together are greater so that the interlayer space is less expandable and the interlayer cations less exchangeable.

Micas (biotite and muscovite) are related to pyrophyllite and talc by substitution of an Al^{3+} for a Si^{4+} in a tetrahedral site. The structure of muscovite is illustrated in Figure 6.26. The result is that the silicate layers are

Table 6.03. Ion Exchange Capacity of Clays.

Smectite	80-150
Vermiculite	120-200
Illite	10-40
Kaolinite	1-10
Chlorite	<10

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The corresponding equilibrium constant expression is written as:

$$K = \frac{a_{Y\text{-clay}} a_{X^+}}{a_{X\text{-clay}} a_{Y^+}} \quad \text{or:} \quad \frac{a_{Y\text{-clay}}}{a_{X\text{-clay}}} = K \frac{a_{Y^+}}{a_{X^+}} \quad 6.90$$

If we express this with molar concentrations in solution and mole fractions (X) in the solid rather than activities:

$$\frac{X_{Y\text{-clay}}}{X_{X\text{-clay}}} = K' \frac{[Y^+]}{[X^+]}$$

K' is called the *selectivity constant*. It expresses the selectivity of the clay for the Y ion over the X ion. Because we have expressed it in mole fraction rather than activity, we can expect its value to depend on the composition of both the clay and the solution. We may also define a *distribution coefficient* K_d as:

$$K_d = \frac{[X_{\text{clay}}]}{[X^+]} \quad 6.91$$

Where Henry's Law holds, K_d should be independent of the concentration of the ion in solution or in the clay, but it will nevertheless depend on the overall composition of the solution and the clay (in other words, the Henry's law constant will be different for different clays and solutions).

A more general expression for the equilibrium constant is:

$$\frac{a_{Y\text{-clay}}^{v_Y}}{a_{X\text{-clay}}^{v_X}} = K \frac{a_{Y^+}^{v_Y}}{a_{X^+}^{v_X}} \quad 6.92$$

where v is the stoichiometric coefficient.

The power term is important. Consider the case of exchange between Na^+ and Ca^{2+} . The reaction is:



The K' expression is:

$$\frac{X_{\text{Ca}^{2+}}}{X_{\text{Na}^+}^2} = K' \frac{[\text{Ca}^{2+}]}{[\text{Na}^+]^2} \quad 6.94$$

If we assume that (1) the mole fractions of Na^+ and Ca^{2+} in the clay must sum to one (i.e., they are the only ions in the exchanging site), (2) molar concentrations of 1 for Na and Ca in solution, and (3) $K' = 1$, solving equation 6.94 yields $X_{\text{Na}} = 0.62$ and $X_{\text{Ca}} = 0.38$. If we kept the ratio of Ca and Na in solution constant, but dilute their concentrations 1000 fold, we obtain $X_{\text{Na}} = 0.03$ and $X_{\text{Ca}} = 0.97$. Thus by diluting the solution, the divalent cation has almost entirely replaced the monovalent ion. The composition of the clay will thus depend on the ionic strength of the solution. The dominant exchangeable cation is Ca^{2+} in fresh water, but Na^+ in seawater.

6.6 MINERAL SURFACES AND THEIR INTERACTION WITH SOLUTIONS

Reactions between solutions and solids necessarily involves the interface between these phases. The details of interface processes thus govern equilibria between solids and solutions. Because clays and other sedimentary particles are typically very small, their surface area to volume ratio is high. This adds to the importance of surface chemistry. For example, the concentrations of many trace elements, particularly the transition metals, dissolved in streams, rivers, and the oceans are controlled not by precipitation and dissolution, but rather by adsorption on and desorption from mineral and organic surfaces. These surface reactions maintain the concentrations of these elements in seawater well below saturation levels. Surface processes also play an important role in soil fertility. Soils have concentrations of many elements above levels one would predict from equilibrium dissolution and precipitation because of adsorption onto particles surfaces. Surface adsorption will also strongly affect the dispersion of pollutants in soils, ground and surface waters. We discussed some aspects of surface

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chemistry in Chapter 5 within the context of kinetic fundamentals. We return to it in this chapter in a broader context.

6.6.1 Adsorption

We can define adsorption as attachment of an ion in solution to a pre-existing solid surface, for example a clay particle. Adsorption involves one or more of the following:

- *Surface complex formation:* The formation of coordinative bonds between metals and ligands at the surface. Considered in isolation, this process is very similar to the formation of complexes between dissolved components.
- *Electrostatic interactions:* As we shall see, solid surfaces are typically electrically charged. This electrostatic force, which is effective over greater distances than purely chemical forces, affects surface complex formation and loosely binds other ions to the surface. For solutions, we were able to make the simplifying assumption of electrical neutrality. We cannot make this assumption about surfaces.
- *Hydrophobic adsorption:* Many organic substances, most notably lipids, are highly insoluble in water due to their non-polar nature. These substances become adsorbed to surfaces, not because they are attracted to the surface, but rather because they are repelled by water.

The interaction of the three effects make quantitative prediction of adsorption behavior more difficult than prediction of complexation in solution. The functional groups of mineral and organic surfaces have properties similar to those of their dissolved counterparts. In this sense, surface complexation reactions are similar to complexation reactions in solution. However, reactions between these surface groups and dissolved species is complicated by the proximity of surface groups to each other, making them subject to long range electrostatic forces from neighboring groups. For example, the surface charge will change systematically as the adsorbed surface concentration of a positive species such as H^+ increases. This change in surface charge will decrease the attraction between H^+ ions and the surface. As a result, the equilibrium constant for the surface protonation reaction will change as the surface concentration of H^+ increases.

We found in Chapter 5 that adsorption is usually described in terms of adsorption isotherms. We introduced two such isotherms, the *Langmuir* isotherm:

$$\Theta_M = \frac{K_{ad}[M]}{1 + K_{ad}[M]} \quad (5.130)$$

(where Θ_M is the fraction of surface sites occupied by species M, $[M]$ is the dissolved concentration of M, and K_{ad} is the adsorption equilibrium constant), and the *Freundlich* isotherm:

$$\Theta_M = K_{ad}[M]^n \quad (5.134)$$

where n is an empirical constant. We derived the Langmuir isotherm from kinetic fundamentals, but we could have also derived it from thermodynamics. Inherent in its derivation are the assumptions that (1) the free energy of adsorption is independent of the number of sites available, and therefore that (2) the law of mass action applies, and that (3) only a monolayer of adsorbate can form. The Langmuir isotherm thus shows a decrease in the fraction of M adsorbed when the concentration of M in solution is high, reflecting saturation of the surface. In contrast, the Freundlich isotherm, which is merely empirical, shows no saturation. We also found that at low relative saturation of the surface, the Freundlich isotherm with $n=1$ approximates the Langmuir isotherm.

Adsorption phenomena can be treated with the *surface complexation model*, which is a generalization of the Langmuir isotherm (Stumm and Morgan, 1996; Morel and Hering, 1993). The model incorporates both *chemical bonding of solute species to surface atoms* and *electrostatic interactions between the surface and solute ions*. The model assumes that these two effects can be treated separately. Thus the free energy of adsorption is the sum of a complexation, or intrinsic, term and an electrostatic, or coulombic term:

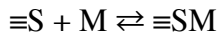
$$\Delta G_{ad} = \Delta G_{intr} + \Delta G_{coul} \quad 6.95$$

From this it follows that the adsorption equilibrium constant can be written as:

$$K_{ad} = K_{intr} K_{coul}$$

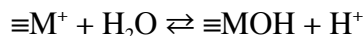
6.96

Letting $\equiv S$ denote the surface site and M denote a solute species, we may write the adsorption reaction as:



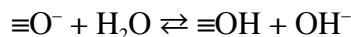
Let's begin by considering comparatively simple surfaces: those of metal oxides. Although silicates are likely to be more abundant than simple oxides, the properties of silicate surfaces approximate those of mixtures of their constituent oxides' surfaces. Hence what we learn from consideration of oxides can be applied to silicates as well. We will initially focus just on the intrinsic terms in equations 6.95 and 6.96. We will return to the coulombic term at the end of this section.

Oxygen and metal atoms at an oxide surface are incompletely coordinated; i.e., they are not surrounded by oppositely charged ions as they would be in the interior of a crystal (Figure 6.28a). Consequently, mineral surfaces immersed in water attract and bind water molecules (Figure 6.28b). These water molecules can then dissociate, leaving a hydroxyl group bound to the surface metal ion. We may write this reaction as:

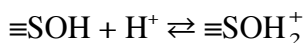


where $\equiv M$ denotes a surface metal ion.

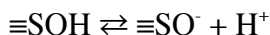
In a similar fashion, incompletely coordinated oxygens at the surface can also bind water molecules, which can then dissociate, again creating a surface hydroxyl group:



Thus the surface on an oxide immersed in water very quickly becomes covered with hydroxyl groups (Figure 6.28c), which we can write as $\equiv SOH$ and which are considered to constitute part of the surface rather than the solution. These hydroxyl groups can then act as either proton acceptors or proton donors through further association or dissociation reactions, e.g.:



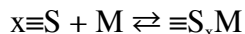
or



We should not be surprised to find that these kinds of reactions are strongly pH dependent.

Adsorption of metals to the surface may occur through replacement of a surface proton, as is illustrated in Figure 6.29a, while ligands may be absorbed by replacement of a surface OH group (Figure 6.29b). The adsorbed metal may bind an additional ligand (Fig. 6.29c), and the adsorbed ligand may bind an additional metal (Fig. 6.29d).

An additional possibility is multidentate adsorption, where a metal or ligand is bound to more than one surface site (Figures 6.29e and 6.29f). This raises an interesting dilemma for the Langmuir isotherm. Where x sites are involved, we could write the reaction as:



and the corresponding equilibrium constant expression as:

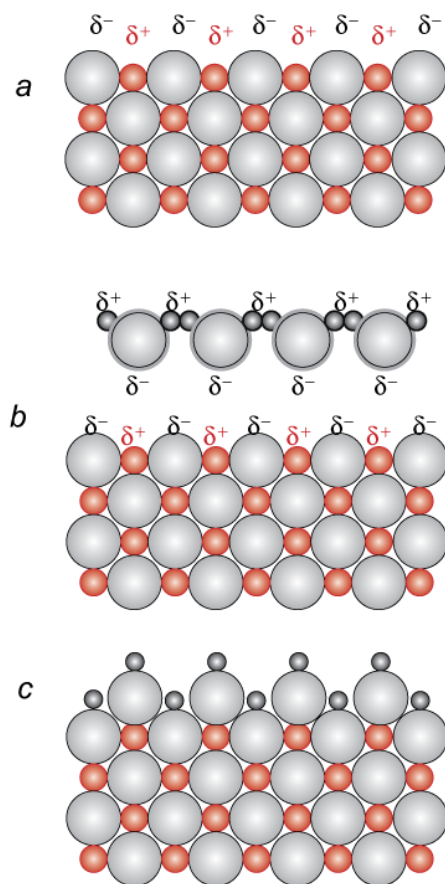


Figure 6.28. (a) Metal ions (small red spheres) and oxygens (large gray spheres) on a mineral surface are incompletely coordinated, leading to a partial charge on the surface (indicated by δ^+ and δ^-). (b) When the mineral surface is immersed in water, water molecules coordinate metal ions on the surface. (c) Water molecules will dissociate leaving hydroxyl groups coordinating metal ions. Protons (small dark spheres) will associate with surface oxygens, forming additional hydroxyl groups.

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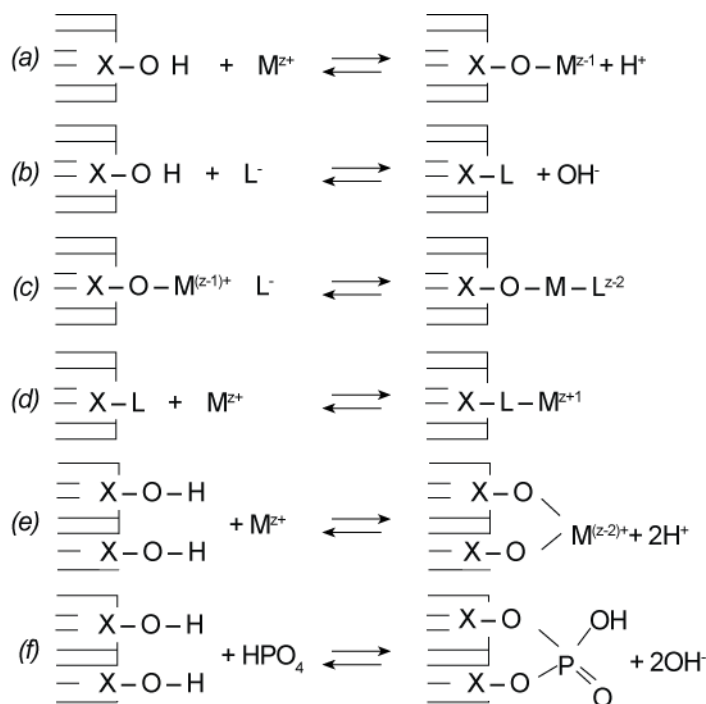


Figure 6.29. Complex formation of solid surfaces may occur when (a) a metal replaces a surface proton, or (b) a ligand replaces a surface OH group. The adsorbed metal (c) may bind an additional ligand, and the ligand (d) may bind an additional metal. Multidentate adsorption involves more than one surface site (e, f).

nearly complete over a very narrow range of pH. This strong dependence on pH certainly reflects protonation of the surface as we have discussed above, but it also reflects the extent of hydrolysis of the ion in solution. We also see that metals vary greatly in how readily they are adsorbed. At a pH of 7, for example, and a solution containing a 1 μM concentration of the metal of interest, the fraction of surface sites occupied by Ca, Ag, and Mn is trivial and only 2% of surface sites would be occupied by Mn and 10% by Cd. At this same pH, however, 97% of sites would be occupied by Pb and essentially all sites would be occupied by Hg and Pd.

As is the case with soluble complexes, surface complexes may be divided into inner sphere and outer sphere complexes (Figure 6.33). Inner sphere complexes involve some degree of covalent bonding between the adsorbed species and atoms on the surface. In an outer-sphere complex, one or more water molecules separate the adsorbed ion and the surface; in this case adsorption involves only electrostatic forces. The third possibility is that an ion may be held within the diffuse layer (see following section) by long-range electrostatic forces.

6.6.2 Development of Surface Charge and the Electric Double Layer

Mineral surfaces develop electrical charge for three reasons:

$$K_{ad} = \frac{[\equiv S_x M]}{[\equiv S]^x [M]} \quad 6.97$$

where x is the number of sites involved and M is the species being adsorbed. This assumes, however, that the probability of finding x sites together is proportional to the x^{th} power of concentration, which is not the case. A better approach is to assume that the reaction occurs with a multidentate surface species, $\equiv S_x$ and that its concentration is $[\equiv S]/x$. The equilibrium constant is then:

$$K_{ad} = \frac{[\equiv S_x M]}{[M][\equiv S]/x}$$

Alternatively, the $1/x$ can be contained within the equilibrium constant.

Since surface bound H^+ and OH^- are almost inevitably involved in adsorption, we would expect that adsorption of metals and ligands will be strongly pH dependent. This is indeed the case, as may be seen in Figure 6.30 and 6.32: adsorption of cations increases with increasing pH while adsorption of anions decreases with increasing pH. Figure 6.32 shows that adsorption of metals on goethite goes from insignificant to

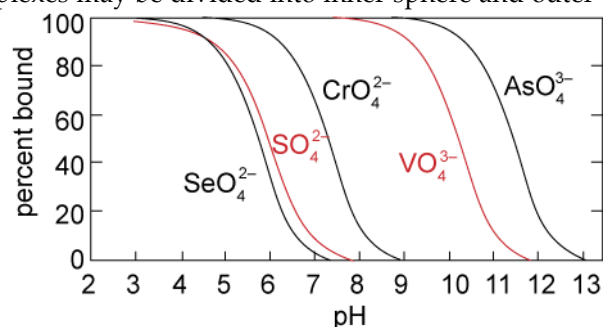


Figure 6.30. Binding of ligands (anions) on the surface of hydrous ferric oxide ($\Sigma\text{Fe} = 10^{-3} \text{ M}$) from dilute solution ($5 \times 10^{-7} \text{ M}$; $I=0.1$) as a function of pH. From Stumm and Morgan (1996).

EXAMPLE 6.11. Adsorption of Pb²⁺ on Hydrous Ferric Oxide as a Function of pH

Using the following apparent equilibrium constants:



calculate the fraction of surface adsorbed Pb as a function of pH from pH 5 to pH 8 for concentrations of surface sites of 10⁻³ M, 10⁻⁴ M, and 10⁻⁵ M assuming a total Pb concentration of 10⁻⁹ M.

Answer: The quantity we wish to calculate is $[\equiv \text{FeOPb}^+] / \Sigma \text{Pb}$, so we want to find an expression for $[\equiv \text{FeOPb}^+]$ as a function of pH. We chose our components to be H⁺, Pb²⁺, and $\equiv \text{FeOH}_2^+$ and begin by writing the two relevant conservation equations:

$$\Sigma \text{Pb} = [\text{Pb}^{2+}] + [\text{PbOH}^+] + [\equiv \text{FeOPb}^+] \quad 6.100$$

$$\Sigma \equiv \text{Fe} = [\equiv \text{FeOH}_2^+] + [\equiv \text{FeOH}] + [\equiv \text{FeO}^-] + [\equiv \text{FeOPb}^+] \quad 6.101$$

From the equilibrium constant expressions, we have the following:

$$[\equiv \text{FeOH}] = \frac{[\equiv \text{FeOH}_2^+]}{[\text{H}^+]} K_{a1} \quad 6.102$$

$$[\equiv \text{FeO}^-] = \frac{[\equiv \text{FeOH}]}{[\text{H}^+]} K_{a2} = \frac{[\equiv \text{FeOH}_2^+]}{[\text{H}^+]^2} K_{a1} K_{a2} \quad 6.103$$

$$[\equiv \text{FeOPb}^+] = [\equiv \text{FeO}^-] [\text{Pb}^{2+}] K_{ad}^{-1} = \frac{[\equiv \text{FeOH}_2^+]}{[\text{H}^+]^2} [\text{Pb}^{2+}] \frac{K_{a1} K_{a2}}{K_{ad}} \quad 6.104$$

Substituting equations 6.102-6.104 into 6.101 we have:

$$\Sigma \equiv \text{Fe} = [\equiv \text{FeOH}_2^+] \left\{ 1 + \frac{K_{a1}}{[\text{H}^+]} + \frac{K_{a1} K_{a2}}{[\text{H}^+]^2} + \frac{[\text{Pb}^{2+}]}{[\text{H}^+]^2} \frac{K_{a1} K_{a2}}{K_{ad}} \right\} \quad 6.105$$

Since the $[\text{Pb}^{2+}]$ is small, the last term on the right can be neglected so we have:

$$\Sigma \equiv \text{Fe} \cong [\equiv \text{FeOH}_2^+] \left\{ 1 + \frac{K_{a1}}{[\text{H}^+]} + \frac{K_{a1} K_{a2}}{[\text{H}^+]^2} \right\}$$

In a similar way, we obtain:

$$\Sigma \text{Pb} = [\text{Pb}^{2+}] \left\{ 1 + \frac{[\equiv \text{FeOH}_2^+]}{[\text{H}^+]^2} \frac{K_{a1} K_{a2}}{[\text{H}^+]^2} + \frac{K_{OH}}{[\text{H}^+]} \right\}$$

Solving this pair of equations for $[\equiv \text{FeOH}_2^+]$ and $[\text{Pb}^{2+}]$, and substituting these into 6.102, we obtain:

$$[\equiv \text{FeOPb}^+] = \frac{[\equiv \text{FeOH}_2^+]}{[\text{H}^+]^2 + [\text{H}^+] K_{a1} + K_{a1} K_{a2}} \left\{ \frac{\Sigma \text{Pb}}{\frac{\Sigma \equiv \text{Fe} K_{a1} K_{a2} / K_{ad}}{[\text{H}^+]^2 + [\text{H}^+] K_{a1} + K_{a1} K_{a2}} + \frac{K_{OH}}{[\text{H}^+]}} \right\} \left(\frac{K_{a1} K_{a2}}{K_{ad}} \right)$$

Dividing by ΣPb and simplifying, we have:

$$\frac{[\equiv \text{FeOPb}^+]}{\Sigma \text{Pb}} = \frac{\Sigma \equiv \text{Fe} K_{a2}}{K_{ad}([\text{H}^+]^2 / K_{a1} + [\text{H}^+] + K_{a2}) + ([\text{H}^+] / K_{a1} + 1 + K_{a2} / [\text{H}^+]) K_{OH} K_{ad} + \Sigma \equiv \text{Fe} K_{a2}}$$

The result is shown in Figure 6.31. For the highest concentration of surface sites, Pb goes from virtually completely in solution to virtually completely adsorbed within 2 pH units.

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1. *Complexation reactions between the surface and dissolved species*, such as those we discussed in the previous section. Most important among these are protonation and deprotonation. Because these reactions depend on pH, this aspect of surface charge is pH dependent. This pH dependence is illustrated in Figure 6.34.
2. *Lattice imperfections* at the solid surface as well as substitutions within the crystal lattice (e.g., Al^{3+} for Si^{4+}). Because the ions in interlayer sites of clays are readily exchangeable, this mechanism is particularly important in the development of surface charge in clays.
3. *Hydrophobic adsorption*, primarily of organic compounds, and “surfactants” in particular. We will discuss this effect in Chapter 14.

Thus there are several contributions to surface charge density. We define σ_{net} as the *net density of electric charge on the solid surface*, and express it as:

$$\sigma_{net} = \sigma_0 + \sigma_H + \sigma_{SC} \quad 6.106$$

where σ_0 is the *intrinsic* surface charge due to lattice imperfections and substitutions, σ_H is the net proton charge, i.e., the charge due to binding H^+ and OH^- , σ_{SC} is the charge due to other surface complexes. σ is usually measured in coulombs per square meter (C/m^2). σ_H is given by:

$$\sigma_H = F(\Gamma_H - \Gamma_{OH}) \quad 6.107$$

where F is the Faraday constant and Γ_H and Γ_{OH} are the adsorption densities (mol/m^2) of H^+ and OH^- respectively. In a similar way, the charge due to other surface complexes is given by

$$\sigma_{SC} = F(z_M \Gamma_M + z_A \Gamma_A) \quad 6.108$$

where the subscripts M and A refer to metals and anions respectively, Γ is again adsorption density and z is the charge of the ion. The surface complex term may also be broken into an inner sphere and outer sphere component:

$$\sigma_{SC} = \sigma_{IS} + \sigma_{OS} \quad 6.109$$

Thus net charge on the mineral surface is:

$$\sigma_{net} = \sigma_0 + F(\Gamma_H - \Gamma_{OH} + Z_M \Gamma_M + Z_A \Gamma_A)$$

Figure 6.34 shows that at some value of pH the surface charge, σ_{net} will be zero. The pH at which this occurs is known as the *isoelectric point*, or *zero point of charge* (ZPC). The ZPC is the pH at which the charge on the surface of the solid caused by binding of all ions is 0, which occurs when the charge due to adsorption of cations is balanced by charge due to adsorption of anions. A related concept is the *point of zero net proton charge* (pznpc), which is the point of zero charge when the charge due to the binding of H^+ and OH^- is 0; i.e., pH where $\sigma_H = 0$. Table 6.4 lists

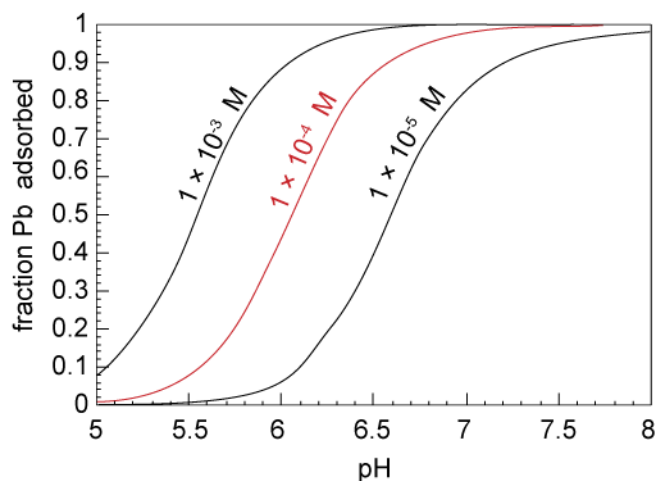


Figure 6.31. Calculated adsorption of Pb^{2+} on hydrous ferric oxide for three different concentrations of surface sites: $10^{-3} M$, $10^{-4} M$, and $10^{-5} M$.

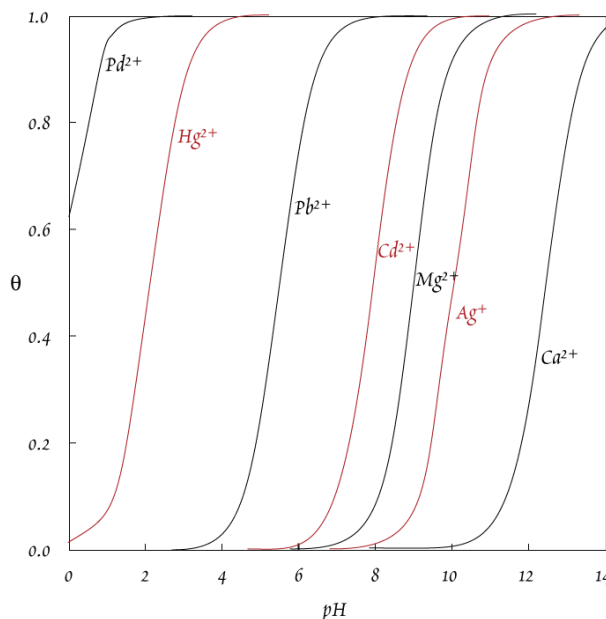


Figure 6.32. Calculated adsorption (θ , fraction of sites occupied) of metals on goethite ($FeOOH$) using adsorption coefficients of Mathur and Dzombak (2006) for a dissolved metal concentration of $10^{-6} M$.

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values of the point of zero net proton condition for some important solids. Surface charge depends on the nature of the surface, the nature of the solution, and the ionic strength of the latter. An important feature of the point of zero charge, however, is that it is independent of ionic strength, as is illustrated in Figure 6.35.

6.6.2.1 Determination of Surface Charge

The surface charge due to binding of protons and hydroxyls is readily determined by titrating a solution containing a suspension of the material of interest with strong acid or base. The idea is that any deficit in H^+ or OH^- in the solution is due to binding with the surface. For example, consider a simple hydroxide surface with surface species $\equiv SOH_2^+$ and $\equiv SO^-$ (as well as $\equiv SOH^0$). Charge balance requires that:

$$C_A - C_B + [OH^-] - [H^+] = [\equiv SOH_2^+] - [\equiv SO^-]$$

where C_A and C_B are the concentrations of conjugate of the acid or base added (e.g., Na^+ is the conjugate of the base $NaOH$) and $[\equiv SOH_2^+]$ and $[\equiv SO^-]$ are the concentrations (in moles per liter) of the surface species. The surface charge, Q (in units of moles of charge per liter), is simply:

$$Q = [\equiv SOH_2^+] - [\equiv SO^-]$$

So that the surface charge is determined from:

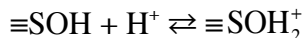
$$Q = C_A - C_B - [H^+] + \frac{10^{-14}}{[H^+]} \quad 6.111$$

The surface charge density, σ , is calculated from Q as:

$$\sigma = \frac{QF}{A[\equiv S]} \quad 6.112$$

where A is the specific surface area (m^2/mol) and $[\equiv S]$ is the concentration of solid (in $mols/l$)*.

We can write equilibrium constant expressions for the surface protonation and deprotonation reactions. For example, for surface protonation:



the equilibrium constant is:

$$K = \frac{[\equiv SOH_2^+]}{[\equiv SOH][H^+]} \quad 6.113$$

We may write a conservation equation for the surface as:

$$\Sigma \equiv S = [\equiv SOH_2^+] + [\equiv SO^-] + [\equiv SOH^0] \quad 6.114$$

At pH below the *pzpc*, we can consider the entire surface charge as due to $[\equiv SOH_2^+]$, so that $Q \approx [\equiv SOH_2^+]$, and $[\equiv SO^-] \approx 0$. Combining equations 6.109, 6.111 and 6.112, we have:

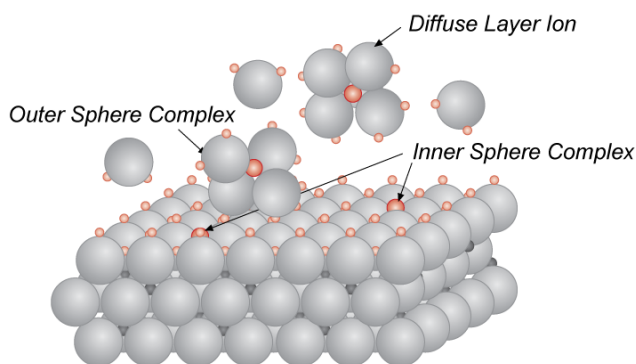


Figure 6.33. Inner sphere surface complexes involve some degree of covalent bonding between the surface and the ion; outer sphere complexes form when one or more water molecules intervenes between the surface and the ion. Ions may also be held in the diffuse layer by electrostatic forces.

Table 6.04. Point of Zero Net Proton Charge of Common Sedimentary Particles

Material	pH
SiO ₂ (quartz)	2.0
SiO ₂ (gel)	1.0-2.5
α-Al ₂ O ₃	9.1
Al(OH) ₂ (gibbsite)	8.2
TiO ₂ (anatase)	7.2
Fe ₃ O ₄ (magnetite)	6.5
α-Fe ₂ O ₃ (hematite)	8.5
FeO(OH) (goethite)	7.8
Fe ₂ O ₃ ·nH ₂ O	8.5
δ-MnO	2.8
β-MnO	7.2
Kaolinite	4.6
Montmorillonite	2.5

From Stumm (1992).

* If the concentration of solid is expressed in kg/l, as it commonly is, then the specific surface area should be in units of m^2/kg .

$$K = \frac{Q}{(\Sigma \equiv S - Q)[H^+]} \quad 6.115$$

In equation 6.111, we see that if the amount of acid (or base) added is known, the surface charge can be determined by measuring pH (from which $[OH^-]$ may also be calculated). This is illustrated in Figure 6.36.

Thus the value of the protonation reaction equilibrium constant may be calculated from the surface charge and pH. The equilibrium constant for the deprotonation reaction may be obtained in a similar way. These equilibrium constants are also known as *surface acidity constants*, and sometimes denoted (as in Example 6.11) as K_{a1} and K_{a2} for the protonation and deprotonation reaction respectively.

6.6.2.2 Surface Potential and the Double Layer

The charge on a surface exerts a force on ions in the adjacent solution and gives rise to an electric potential, Ψ (measured in volts), which will in turn depend on the nature and distribution of ions in solution, as well as intervening water molecules. The surface charge results in an excess concentration of oppositely charged ions (and a deficit of liked charged ions) in the immediately adjacent solution.

The surface charge, σ , and potential, Ψ_0 , can be related by *Gouy-Chapman Theory*[‡], which is conceptually and formally similar to Debye-Hückel Theory (Chapter 3). The relationship between surface charge and the electric potential is:

$$\sigma = (8RT\epsilon_r\epsilon_0 I)^{1/2} \sinh\left(\frac{z\Psi_0 F}{2RT}\right) \quad 6.116$$

where z is the valence of a symmetrical background electrolyte (e.g., 1 for NaCl), Ψ_0 is the potential at the surface, F is the Faraday constant, T is temperature, R is the gas constant, I is ionic strength of the solution in contact with the surface, ϵ_r

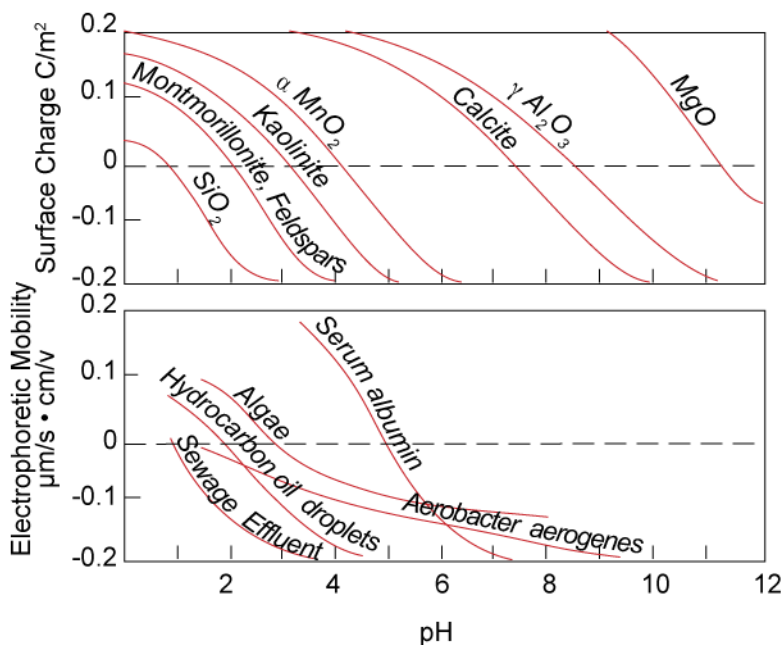


Figure 6.34. (a) Surface charge of some common sedimentary materials as a function of pH. (b) Electrophoretic mobility, which is related to surface charge, of representative organic substances as a function of pH. The pH dependence of surface charge reflects the predominance of attached protons at low pH and the predominance of attached hydroxyls at higher pH. From Stumm (1992).

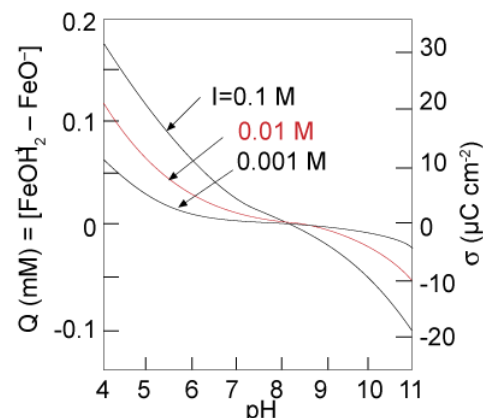


Figure 6.35. Surface charge on FeOOH as a function of pH for different ionic strengths of a 1:1 electrolyte (10^{-3} M FeOOH). From Dzombak and Morel (1990).

[‡] Gouy-Chapman Theory assumes an infinite flat charge plane in one dimension. The electrostatic interaction between the surface and a cloud of charged particles is described by the Poisson-Boltzmann equation, as in Debye-Hückel Theory. Unlike Debye-Hückel, the Poisson-Boltzmann equation has an exact solution in this case. The theory was developed by Gouy and Chapman around 1910, a decade before Debye and Hückel developed their theory. See Morel and Herring (1993) for the details of the derivation.

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is the dielectric constant of water and ϵ_0 is the permittivity of a vacuum (see Chapter 3). At 25°C, equ. 6.116 may be written as:

$$\sigma = \alpha l^{1/2} \sinh(\beta z \Psi_0) \quad 6.117$$

where α and β are constants with value of 0.1174 and 19.5 respectively.

Where the potential is small, the potential as a function of distance from the surface is:

$$\Psi(x) = \Psi_0 e^{-\kappa x} \quad 6.118$$

where κ has units of inverse length and is called the Debye parameter or Debye length and is given by:

$$\kappa = \sqrt{\frac{2F^2 I}{\epsilon_r \epsilon_0 RT}} \quad 6.119$$

From equation 6.118, we see that the inverse of κ is the distance at which the electrostatic potential will decrease by 1/e. The variation in potential, the Debye length, and the excess concentration of counter-ions with distance from the surface is illustrated in Figure 6.37.

An addition simplification occurs where the potential is small, namely that equation 6.116 reduces to:

$$\sigma = \epsilon \epsilon_0 \kappa l^{2/3} \Psi_0$$

As is illustrated in Figure 6.37, an excess concentration of oppositely charged ions develops adjacent to the surface. Thus an *electric double layer* develops adjacent to the mineral surface. The inner layer, or Stern Layer[†], consists of charges fixed to the surface, the outer diffuse layer, or Gouy Layer, consists of dissolved ions that retain some freedom of thermal movement. This is illustrated in Figure 6.38. The Stern Layer is sometimes further subdivided into an inner layer of specifically adsorbed ions (inner sphere complexes) and an outer layer of ions that retain their solvation shell (outer sphere complexes), called the inner and outer Helmholtz planes respectively. Hydrogens adsorbed to the surface are generally considered to be part of the solid rather than the Stern Layer. The thickness of the Gouy (outer) Layer is considered to be the Debye length, $1/\kappa$. As is apparent in equation 6.119, this thickness will vary inversely with the square root of ionic strength. Thus the Gouy Layer will collapse in high ionic strength solutions and expand in low ionic strength ones.

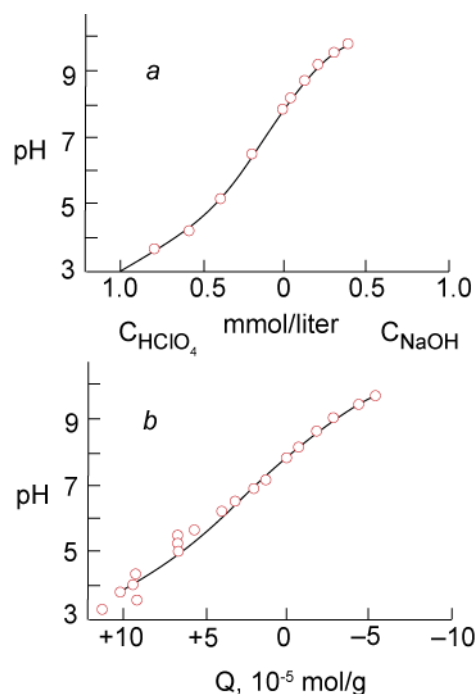


Figure 6.36. (a). Titration of a suspension of α -FeOOH (goethite) (6 g/liter) by HClO₄ and NaOH in the presence of 0.1 M NaClO₄. (b). Charge calculated by charge balance (equation 6.109) from the titration. From Stumm (1992).

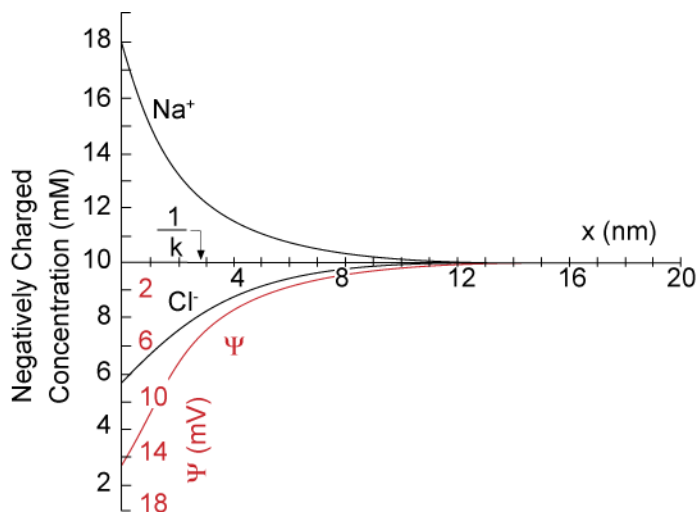


Figure 6.37. Variation in electrical potential and ions with distance from a negatively charged surface based on the Gouy-Chapman model. Electrical potential varies exponentially with distance, as do ion concentrations. $1/\kappa$ is the distance where the potential has decreased by 1/e. From Morel and Hering (1993).

[†] This fixed layer is also sometimes called the Helmholtz Layer, after Herman von Helmholtz (1821-1894), who first proposed it (and for whom the Helmholtz Free Energy is also named).

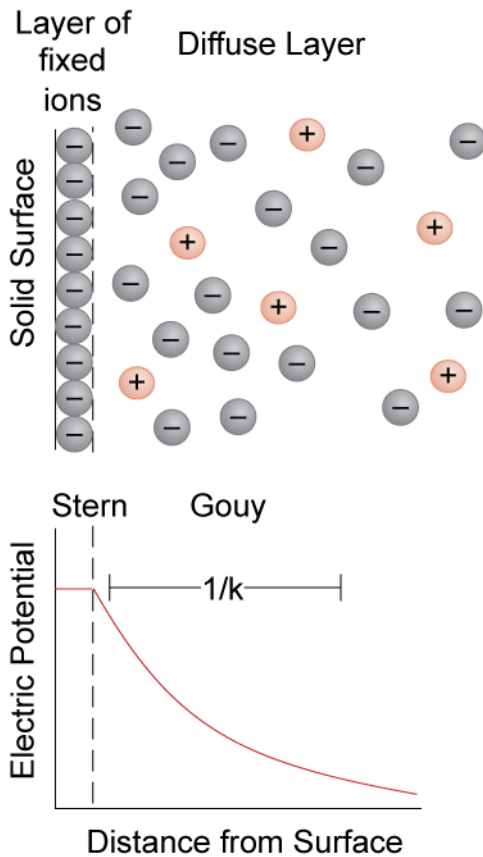


Figure 6.38. The double layer surrounding clay particles.

can participate in surface reactions. We can account for this effect by including it in the Gibbs Free Energy of reaction, as in equation 6.95:

$$\Delta G_{\text{ads}} = \Delta G_{\text{intr}} + \Delta G_{\text{coul}} \quad (6.95)$$

where ΔG_{ads} is the total free energy of the adsorption reaction, ΔG_{intr} is the *intrinsic* free energy of the reaction (i.e., the value the reaction would have in the absence of electrostatic forces; in general this will be similar to the free energy of the same reaction taking place in solution), and ΔG_{coul} is the free energy due to the electrostatic forces and is given by:

$$\Delta G_{\text{coul}} = F\Delta Z\Psi_0 \quad 6.120$$

where ΔZ is the change in molar charge of the surface species due to the adsorption reaction. For example, in the reaction:

When clays are strongly compacted, the Gouy layers of individual particles overlap and ions are virtually excluded from the pore space. This results in retardation of diffusion of ions, but not of water. As a result, clays can act as *semi-permeable membranes*. Because some ions will diffuse easier than others, a chemical fractionation of the diffusing fluid can result.

At low ionic strength, the charged layer surrounding a particle can be strong enough to repel similar particles with their associated Gouy layers. This will prevent particles from approaching closely and hence prevent coagulation. Instead, the particles form a relatively stable *colloidal* suspension. As the ionic strength of the solution increases, the Gouy layer is compressed and the repulsion between particles decreases. This allows particles to approach closely enough that they are bound together by attractive van der Waals forces between them. When this happens, they form larger aggregates and settle out of the solution. For this reason, clay particles suspended in river water will flocculate and settle out when river water mixes with seawater in an estuary.

6.6.2.3 Effect of the Surface Potential on Adsorption

The electrostatic forces also affect complexation reactions at the surface, as we noted at the beginning of this section. An ion must overcome the electrostatic forces associated with the electric double layer before it

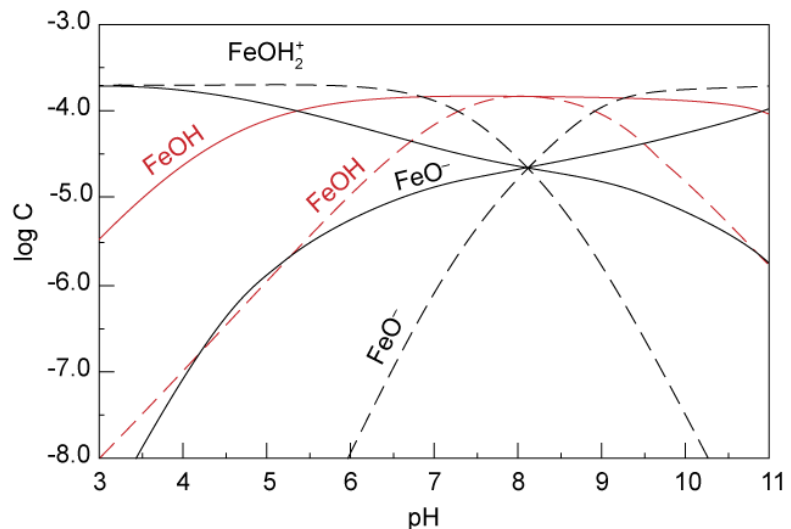
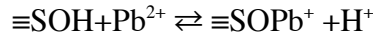


Figure 6.39. Surface speciation of hydrous ferric oxide for $I = 0.1$ M calculated in Example 6.11. Solid lines show speciation when surface potential term is included, dashed lines show the calculated speciation with no surface potential.



the value of ΔZ is +1 and $\Delta G_{\text{coul}} = \mathcal{F}\Psi$.

Thus if we can calculate ΔG_{coul} , this term can be added to the intrinsic ΔG for the adsorption reaction

Example 6.12. Effect of Surface Potential on Surface Speciation of Ferric Oxide

Using the surface acidity constants given in Example 6.10, calculate the surface speciation of hydrous ferric oxide as a function of pH in a solution with a background electrolyte concentration of $I = 0.1$ M. Assume the concentration of solid is 10^{-3} mol/l, the specific surface area is 5.4×10^4 m²/mol and that there are 0.2 mol of active sites per mole of solid.

Answer: The concentration of surface sites, $\Sigma \equiv \text{Fe}$, is 0.2 mol sites/mol solid $\times 10^{-3}$ mol solid/l = 2×10^{-4} mol sites/l. Our conservation equation is:

$$\Sigma \equiv \text{Fe} = [\equiv \text{FeOH}_2^+] + [\equiv \text{FeOH}] + [\equiv \text{FeO}^-] = 2 \times 10^{-4}$$

We define P as:

$$P = e^{-\mathcal{F}\Delta Z\Psi_0/RT} \tag{6.121}$$

so that our equilibrium constant expressions (6.98 and 6.99) become:

$$[\equiv \text{FeOH}] = \frac{[\equiv \text{FeOH}_2^+]}{[\text{H}^+]} K_{a1} P^{-1} \tag{6.122}$$

and

$$[\equiv \text{FeO}^-] = \frac{[\equiv \text{FeOH}]}{[\text{H}^+]} K_{a2} P^{-1} = \frac{[\equiv \text{FeOH}_2^+]}{[\text{H}^+]^2} K_{a1} K_{a2} P^{-2} \tag{6.123}$$

Substituting into our conservation equation, and solving for $[\equiv \text{FeOH}_2^+]$ we have:

$$[\equiv \text{FeOH}_2^+] = \Sigma \equiv \text{Fe} \left\{ 1 + \frac{K_{a1} P^{-1}}{[\text{H}^+]} + \frac{K_{a1} K_{a2} P^{-2}}{[\text{H}^+]^2} \right\} \tag{6.124}$$

The concentration of surface charge, Q , is simply: $Q = [\equiv \text{FeOH}_2^+] - [\equiv \text{FeO}^-]$

and the surface charge density is: $\sigma = \frac{\mathcal{F}}{A[S]} ([\equiv \text{FeOH}_2^+] - [\equiv \text{FeO}^-])$

(P enters the equations as the inverse because we have defined the equilibrium constants in Example 6.11 for the *desorption* reactions.) Substituting into the surface charge density equation, we have:

$$\sigma = \frac{\mathcal{F}}{A[S]} [\equiv \text{FeOH}_2^+] \left\{ 1 - \frac{K_{a1} K_{a2} P^{-2}}{[\text{H}^+]^2} \right\} \tag{6.125}$$

Substitution equation 6.124 into 6.125, we have:

$$\sigma = \frac{\mathcal{F}}{A[S]} \Sigma \equiv \text{Fe} \left\{ 1 + \frac{K_{a1} P^{-1}}{[\text{H}^+]} + \frac{K_{a1} K_{a2} P^{-2}}{[\text{H}^+]^2} \right\}^{-1} \left\{ 1 - \frac{K_{a1} K_{a2} P^{-2}}{[\text{H}^+]^2} \right\} \tag{6.126}$$

Finally, substituting equation 6.117 for σ , and 6.123 for P , we have:

$$\sinh(\beta z \Psi_0) = \frac{\mathcal{F}}{A[S] \alpha I^{1/2}} \Sigma \equiv \text{Fe} \frac{\left\{ 1 - \frac{K_{a1} K_{a2} e^{2\mathcal{F}\Delta Z\Psi_0/RT}}{[\text{H}^+]^2} \right\}}{\left\{ 1 + \frac{K_{a1} e^{\mathcal{F}\Delta Z\Psi_0/RT}}{[\text{H}^+]} + \frac{K_{a1} K_{a2} e^{2\mathcal{F}\Delta Z\Psi_0/RT}}{[\text{H}^+]^2} \right\}} \tag{6.127}$$

A pretty intimidating equation, and one with no direct solution. It can, however, be solved by indirect methods (i.e, iteratively) on a computer. A quick an easy way is to use the Solver feature in Microsoft Excel™. Figure 6.39 shows the results and compares them to the surface speciation when surface potential is not considered. The effect of including the surface potential term is to reduce the surface concentration of $\equiv \text{FeO}^-$ and $\equiv \text{FeOH}_2^+$, and broaden the pH region where $\equiv \text{FeO}$ dominates.

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(ΔG_{intr}) to obtain the effective value of ΔG (ΔG_{ads}). From ΔG_{ads} it is a simple and straightforward matter to calculate K_{ads} . From equation 3.86 we have:

$$K = e^{-\Delta G_{\text{ads}} / RT}$$

Substituting equation 6.96, we have:

$$K = e^{-\Delta G_{\text{ads}} / RT} e^{\Delta G_{\text{coul}} / RT} \quad 6.128$$

Since $K_{\text{intr}} = e^{\Delta G_{\text{intr}} / RT}$ and $\Delta G_{\text{coul}} = F\Delta Z\Psi_0$, we have:

$$K = K_{\text{intr}} e^{-F\Delta Z\Psi_0 / RT} \quad 6.129$$

Thus we need only find the value of Ψ_0 , which we can calculate from σ using equation 6.114. Example 6.12 illustrates the procedure.

The effect of surface potential on a given adsorbate will be to shift the adsorption curves to higher pH for cations and to lower pH for anions. Figure 6.40 illustrates the example of adsorption of Pb on hydrous ferric oxide. When surface potential is considered, adsorption of a given fraction of Pb occurs at roughly 1 pH unit higher than in the case where surface potential is not considered. In addition, the adsorption curves become steeper.

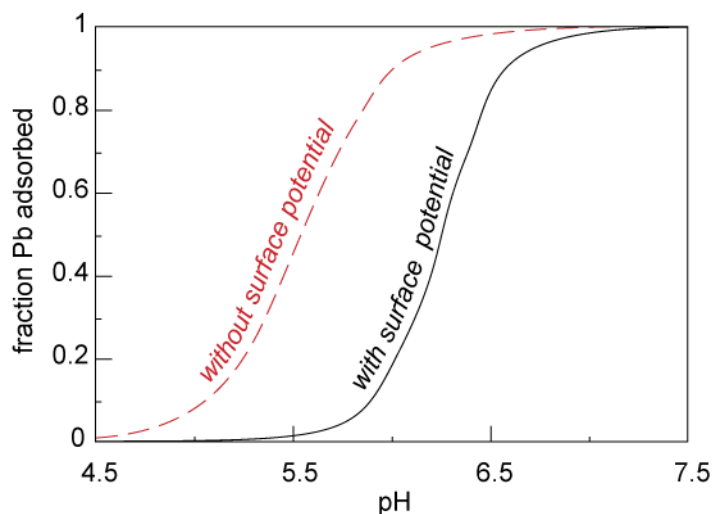


Figure 6.40. Comparison of calculated adsorption of Pb on hydrous ferric oxide with and without including the effect of surface potential.

References and Suggestions for Further Reading

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Problems

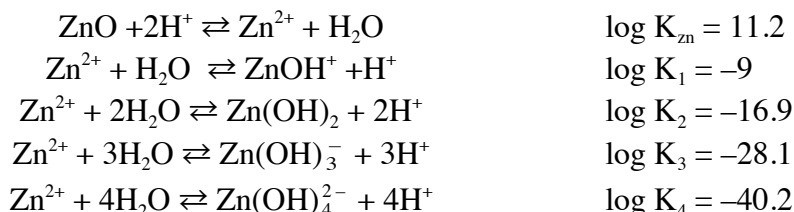
1. Make a plot similar to Figure 6.1, but for water in equilibrium with atmospheric CO_2 ($P_{\text{CO}_2} = 10^{-3.43}$). Assume ideality and that there are no other species present in solution but those shown on the graph.

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What is the pH of the CO₂ equivalence point in this case? What is the pH of the bicarbonate equivalence point?

2. Using the composition given in Problem 3.4, calculate the alkalinity of seawater at 25°C.
3. For a sodium carbonate solution titrated with HCl to the bicarbonate equivalence point, show that:

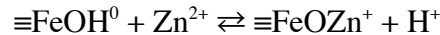
$$\Sigma\text{CO}_2 \cong [\text{Cl}^-] + [\text{OH}^-]$$
4. Calculate the pH of a solution containing $\Sigma\text{CO}_2 = 10^{-2}$ at 25°C at the bicarbonate and carbonate equivalence points. Assume ideality and use the equilibrium constants in Table 6.1.
5. Consider a 0.005M solution of Na₂CO₃ at 25°C. Assuming ideality and that the system is closed:
 - a. What is the pH of this solution?
 - b. What is the pH of this solution when titrated to the bicarbonate equivalence point?
 - c. What is the pH of this solution when titrated to the CO₂ equivalence point?
6. Consider a 0.01M solution of NaHCO₃ (sodium bicarbonate) at 20°C. Assuming ideality:
 - a. What is the pH of this solution?
 - b. Plot the titration curve for this solution (i.e., moles of HCl added vs. pH).
 - c. What is the pH of the CO₂ equivalence point of this solution?
7. Explain why pH changes rapidly near the bicarbonate and CO₂ equivalence points during titration.
8. Mars probably once had a more substantial atmosphere and water on its surface. Suppose that it had a surface atmospheric pressure of 1 bar (0.1 MPa) and that the partial pressure of CO₂ was the same as it is today, 6×10^{-3} . Further suppose the surface temperature was 5° C. Assume ideal behavior and use the equilibrium constant in Table 6.1 for this problem. Under these conditions, at what concentration of Ca²⁺ ion would an ancient Martian stream become saturated with CaCO₃? What would the pH of that stream be? Assume that calcium, carbonate species, and the dissociate products of water are the only ions present.
9. Calculate the buffer capacity of a solution initially in equilibrium with calcite for pH between 6 and 9 at 25°C.
10. Calculate the calcium ion concentration for a solution in equilibrium with calcite and fixed ΣCO_2 of 10⁻² M at 25°C.
11. Show that the α , fraction of copper complexed as CuOH⁺, as defined in equation 6.50, will decrease with increasing concentration of total copper in solution. Assume ideal behavior and that H⁺, OH⁻, Cu²⁺ and CuOH⁺ are the only ions present in solution and that the stability constant of CuOH⁺ is 10⁻⁸.
12. Using the following equilibrium constants and reactions, make a plot of Zn²⁺, ZnOH⁺, Zn(OH)₂, Zn(OH)₃⁻, Zn(OH)₄²⁻, and total zinc concentration as a function of pH from pH 1 to pH 14. Assume ideal behavior and that H⁺, OH⁻, and various species of Zn are the only ions in solution. *Hint: Use a log scale for the Zn concentrations.*



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13. Using the reactions and stability constants given by equations 6.60-6.62, derive the equations used to construct the stability diagram shown in Figure 6.13b. Assume a fixed Mg^{2+} concentration of 10^{-7} M, that the solution is ideal, and that the solids are pure phases.

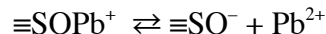
14. For the adsorption of Zn^{2+} on hydrous ferric oxide:



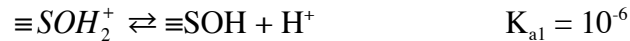
the apparent equilibrium constant is $10^{0.99}$. For this problem, use the surface acidity constants (i.e., equilibrium constants for adsorption and desorption of H^+) given in equations 6.98 and 6.99 (Example 6.10).

- Make a plot of Θ_{Zn} (fraction of sites occupied by Zn) vs. the aqueous concentration of Zn^{2+} (use $\log [Zn^{2+}]$) at pH 7 and a total concentration of surface sites of 10^{-3} M. Assume that Zn^{2+} forms no complexes in solution.
- Ignoring electrostatic effects and any aqueous complexation of Zn^{2+} , make a plot of the fraction of Zn^{2+} adsorbed as a function of pH (from pH 2 to pH 6), assuming a total Zn^{2+} concentration of 10^{-8} M.
- Do the same calculation as in b, but take into consideration the aqueous complexation reactions and equilibrium constants in Problem 11.

15. For the adsorption of Pb^{2+} on aluminum oxide:



the apparent equilibrium constant, K_{ad} , is $10^{-6.1}$. In addition, consider the reaction:



Make a plot of the fraction of Pb adsorbed as a function of pH from pH=4 to pH = 7, assuming a total concentration of alumina of 10^{-2} M, a surface site density of 1×10^{-2} moles/mole Al_2O_3 , and total Pb concentration of 10^{-9} M, ignoring electrostatic effects and any complexation in solution. (*Hint* Θ_{Pb} , the fraction of sites occupied by Pb will be negligible).

16. Consider a 10^{-3} M suspension of aluminum oxide (Al_2O_3) in a 1:1 electrolyte having a specific surface area of $500 \text{ m}^2/\text{g}$. At pH 7, the surface charge, Q , is found to be 7.93×10^{-5} moles/l. What is the surface charge density, σ ? If the temperature is 25°C and ionic strength, I , is 10^{-3} M, what is the surface potential, Ψ_0 ? What is the potential at a distance of 1 Debye length from the surface? Make a plot of how Ψ_0 and the Debye length change as I varies from 10^{-3} to 1 (equivalent to going from river water to seawater).