

SOLUBILITY OF SOIL COMPONENTS

Weathering of soil minerals releases Si, Al, and other ions into solution. The extent of mineral weathering is determined by and in turn determines soil solution composition. The inherent solubility of the soil minerals varies for each mineral; however, equilibrium solutions must have a unique composition determined by the simultaneous equilibria among all solids. At this juncture, we will examine the solubility of soil minerals and methods of describing this behavior. Soil minerals like any other chemical compound exhibit some solubility in water. They are mostly sparingly to very slightly soluble compounds but they do dissolve and given geologic time, they will disappear or form alternative stable phases. Since the minerals were formed at high temperature and pressure, they are unstable at the earth's surface. In the surface and near surface environment they will dissolve or weather. Alternatively, we can say that minerals weather because the reaction products have less free energy than the reactants. If we can write a reaction for the weathering or dissolution, then we can express the reaction in an equilibrium expression that, if we are lucky, will have a known equilibrium constant. Solubility of solids vary considerably, for example, sodium salts are generally soluble, while salts of Fe, Al, and Cr are much less soluble. Before we discuss the solubility of soil minerals, it might be instructive to consider the topic in general using the very soluble salt sodium chloride.

Solubility of NaCl in Water - Considerable quantities of NaCl can dissolve in water to yield Na ions and chloride ions. From a quantitative stand point we can write the stoichiometric equation that says: one mole of NaCl yields one mole of sodium ions and one mole of chloride ion:



Such an equation does not relay any details on the quantity of NaCl that dissolves. We must write an equilibrium expression for the dissolution reaction and evaluate the constant to develop a quantitative answer for the amount of dissolved Na and Cl. A solubility expression is a special case of an equilibrium expression where the activity ratio of products to reactants is equal to the equilibrium constant. In this case, the solubility constant is:

$$K_{sp} = \frac{a_{\text{Na}^{+}} a_{\text{Cl}^{-}}}{a_{\text{NaCl}_{(c)}}}$$

In the case where solid $\text{NaCl}_{(c)}$ is present the activity of the pure solid is set equal to 1 and the expression becomes:

$$K_{sp} (a_{\text{NaCl}_{(c)}}) = a_{\text{Na}^{+}} a_{\text{Cl}^{-}}$$

With the solubility constant rearranged, as shown, it becomes evident that: (1) When the solid is present, the activity of sodium times the activity of chloride (IAP of the electrolyte) is fixed and only varies with the activity of the solid; (2) When the solid is not present, the IAP of NaCl is not fixed and is not equal to K_{sp} . [Note that the IAP can still be calculated and has meaning.]

In mathematical terms the activity of Na time the activity of Cl is equal to a constant and has the form:

$$K = (X)(Y)$$

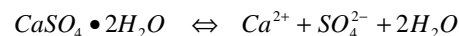
which is the equation for a curve that is asymptotic to the x and y axis as either x or y goes to zero. From a chemical perspective, this means that an IAP for NaCl can be calculated by multiplying the activity of **free** dissolved Na^+ from **all** sources by the activity of **free** Cl from **all** sources. At saturation, the IAP must equal the K_{sp} . This seemingly simple relationship has wide application in soil and aquatic chemistry. Since solution levels of dissolved ions can vary over wide ranges, it is often easier to transform activity (and concentration) values to common logs. In this case the expression becomes a linear equation:

$$\log K = \log (\text{Na}) + \log (\text{Cl}) ; \text{ or more generally: } \log K = \log X + \log Y$$

Sodium chloride is a very soluble salt and only in extreme cases does the solution phase composition approach saturation. This same approach can be applied to salt that are less soluble.

SOLUBILITY OF SLIGHTLY SOLUBLE SALTS

Gypsum is a salt this is considerably less soluble than sodium chloride. It is also a common salt in arid region soils and is used extensively as a soil amendment to increase infiltration. Gypsum (calcium sulfate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is also used in the reclamation of salt affected soils. The following discussion presents a graphical method to compute the activities of Ca and SO_4 knowing the solubility product and the level of Ca or SO_4 . While the example is quite simple, it serves to illustrate the general principles that can be applied to more complex systems.



$$K_{sp} = (Ca_{aq}^{2+})(SO_{4(aq)}^{2-})$$

Taking the logs of both sides gives :

$$\log K_{sp} = \log (Ca_{aq}^{2+}) + \log (SO_{4(aq)}^{2-})$$

Knowing this relationship the log of Ca or SO₄ activity can be plotted as a linear function by rearranging to isolate either log Ca or log SO₄. This example illustrates the general method to graphically present solubility data. The technique is :

1. Write the solubility relationship.
2. Write down the K_{sp}
3. Solve for the required variable by algebraic manipulation of the equations. For sparingly soluble compounds, the solubility of the material itself may be sufficient to increase ionic strength to the point that activity corrections are necessary. Note also, that the number of variables and the number of equations must be equal.
4. Plot the variable in relation to an independent variable. In cases where there are more than one variable, the values of the other variables must be known or assumed to be a known value.
5. The resulting line is defined by the solubility expression. Therefore, this line and values represented by the line represent solubility equilibrium in the system being considered. Data that does not correspond with the line represent ***nonequilibrium*** situations.

There are many reasons that data does not correspond with calculated lines. We will be examining these reasons throughout the course.

In the next section, we will apply the techniques described above to the solubility of the aluminum hydroxide mineral gibbsite.

GIBBSITE SOLUBILITY

Gibbsite is a specific crystal form of aluminum hydroxide. Aluminum hydroxides are very insoluble around neutrality and their solubility increases rapidly as pH decreases.

For the reaction $\text{Al(OH)}_{3(s)} = \text{Al}^{3+} + 3 \text{OH}^-$ the equilibrium expression is:

$$K_{\text{equil}}^{\circ} = \frac{a_{\text{Al}^{3+}} a_{\text{OH}^-}^3}{a_{\text{Al(OH)}_3}}$$

Remembering that the activity of the solid phase is set equal to one, the K_{sp} for zero ionic strength is:

$$K_{\text{sp}}^{\circ} = (\text{Al}) (\text{OH})^3$$

This solubility expression can be manipulated and combined with the hydrolysis constant of water K_w to give an equation in H⁺ and Al³⁺ if the K_{sp}° is known. *Note: this formulation implicitly assumes the activity of the solid is 1 and present in excess.*

$$(\text{Al}^{3+}) = \frac{K_{sp}^o}{(\text{OH}^-)^3} ; \quad (\text{Al}^{3+}) = \frac{K_{sp}^o}{\left[\frac{K_w}{(\text{H}^+)} \right]^3}$$

Rearranging :

$$(\text{Al}^{3+}) = \left[\frac{K_{sp}^o}{K_w^3} \right] * (\text{H}^+)^3$$

Taking the log:

$$\log(\text{Al}^{3+}) = \log \left[\frac{K_{sp}^o}{K_w^3} \right] + \log(\text{H}^+)^3$$

Converting log H to pH :

$$\log(\text{Al}^{3+}) = \log \left[\frac{K_{sp}^o}{K_w^3} \right] - 3 \text{ pH}$$

This is a linear equation in pH and $\log(\text{Al}^{3+})$ with slope of -3 and an intercept of $\log [K_{sp}^o/(K_w)^3]$. Therefore, $\log(\text{Al}^{3+})$ changes by a factor of 3 (or 1000 fold) for each unit change in pH. It is easy to see why pH is such an important variable affecting (Al^{3+}) levels in soils, sediments and solutions.

GRAPHICAL REPRESENTATION OF THE GIBBSITE SOLUBILITY

The equation for Al^{3+} in solution in log form is a linear equation in the variables pH and $\log(\text{Al}^{3+})$ as discussed previously and as shown below.

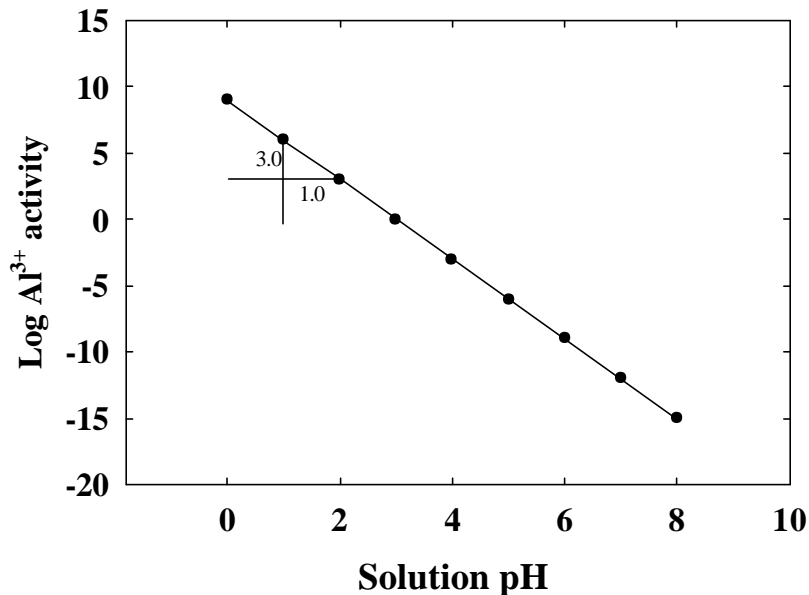
$$\log \text{Al}^{3+} = \log \left[\frac{K_{sp}^o}{K_w^3} \right] - 3 \text{ pH}$$

Thus, the equation is of the form:

$$y = a + bx$$

Where the intercept (a) is ($\log K_{sp}^o/K_w^3$) and the slope (b) is - 3. A plot of this relationship in relation to pH is illustrated below.

Figure 4.1. The relationship of Al^{3+} activity in relation to solution pH.



In Figure 4.1 the line is calculated from a rearrangement of the equilibrium expression. Any point falling on the line represents the activity of Al^{3+} in equilibrium with solid phase Gibbsite. Any other point is not at equilibrium for reasons which may or may not be easily explained. If the point falls above the theoretical equilibrium line, the solution is said to be, “supersaturated”, while points below the line are considered “undersaturated” with respect to the solid phase Gibbsite. A term, the saturation index SI, is used to express the relationship between the theoretical line and experimental values of the ion activity product, IAP. The IAP is another way of expressing the equilibrium constant, which for this reactions is :

$$a_{Al^{3+}} * a_{OH^-}^3 = K_{sp}$$

The Saturation Index (SI) is defined as:

$$\log \left(\frac{IAP}{K_{sp}} \right)$$

If the K_{sp} is equal to the IAP, then the saturation index is zero, supersaturation is represented by a $SI > 0$ and undersaturation by an $SI < 0$.

The Gibbsite case is a simple graphical representation of equilibrium over several values of pH. Application of this technique to any other chemical reaction is carried out in the same way. Complications arises when there are more than one variable in the equation. In these cases: (1) a three dimensional graph can be used; (2) one axis can contain a combination of variable such as (pH + Al); or (3) one variable can be fixed by assuming a value for that particular component. Lets consider an example described in McBride (1994).

Kaolinite [$Al_2Si_2O_5(OH)_4$] in the presence of water dissolves to give aluminum ions, silicic acid and water:



The equilibrium expression for this reaction is:

$$\frac{(Al^{3+})^2 (H_4SiO_4)^2}{(H^+)^6 (Al_2Si_2O_5(OH)_4)} = K_{dissol} \quad (2)$$

Taking the logs of the expression and recognizing that the activity of the solid species is 1, results in the following:

$$2 \log(Al^{3+}) - 6 \log(H^+) = \log K_{dissol} - 2 \log(H_4SiO_4) \quad (3)$$

$$\log(Al^{3+}) + 3pH = \frac{\log K_{dissol}}{2} - \log(H_4SiO_4)$$

If K_{dissol} is known (in this case $\log K_{dissol} = 7.63$, then dividing and simplifying yields :

$$\log Al^{3+} = 3.81 - \log H_4SiO_4 - 3pH \quad (4)$$

Equation (4) represents a plane in pH, log Al, and log H_4SiO_4 space and is the equilibrium expression for the above reaction. (see Fig 6.13 in McBride, and appendix 3.1 in Bohn for examples of these plots and Figure 4.3 in Sparks.). The two dimensional case where H_4SiO_4 is fixed is plotted on page 7. As with the Gibbsite case analytical values below the plane represent supersaturation ($SI > 0$), while those above the plane represent undersaturation ($SI < 0$). Note well, that an IAP can be calculated regardless of whether the solution is at equilibrium, supersaturated or undersaturated. As you can imagine, the graph could be a two dimensional plot if the concentration of Al, H, or Si were fixed at some arbitrary value. Whether the real

world is at equilibrium or ever approaches these values has been debated for some time. However, the diagrams do provide a convenient estimate of reactions and their probabilities in the soil system. We encounter these representations in the sections on buffering, carbonate equilibria, and mineralogy. The concepts will be elaborated upon in the next section on solutions.

Figure 4.2. The stability diagram for kaolinite at a fixed silicic acid level of 1 mM.

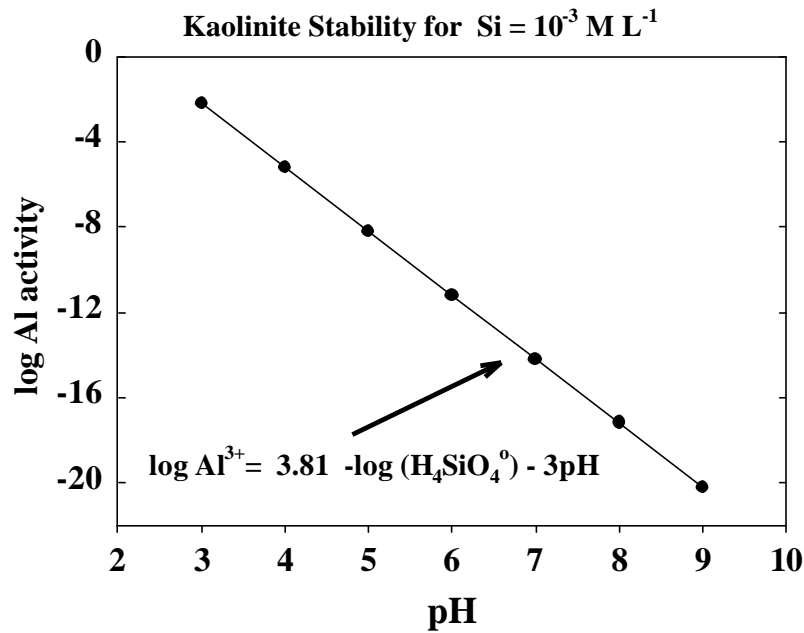
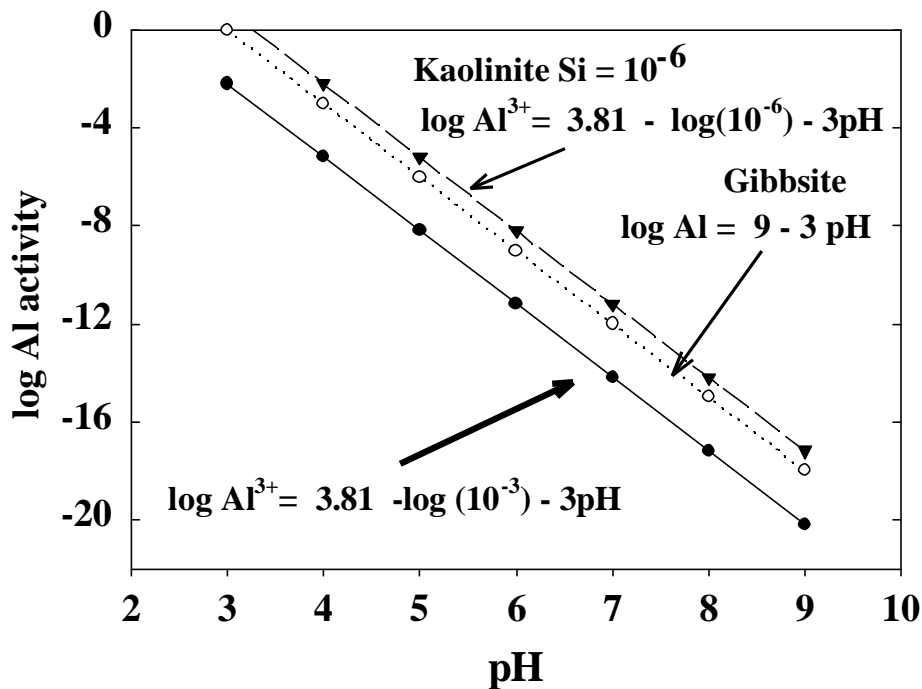


Figure 4.3 The stability of kaolinite at two levels of Si in comparison to gibbsite.



Appendix 4.1

An example of using free energies to derive equilibrium constants.

It is known from thermodynamics that for any reactions at constant temperature and pressure the free energy (G°) is the algebraic sum of the difference between the products and the reactants:

$$\Delta G_{\text{Reaction}}^\circ = \Delta G_{\text{Products}}^\circ - \Delta G_{\text{Reactants}}^\circ \quad (1)$$

Thermochemistry also tells us that equilibrium constants and free energy are related via (2).

$$\Delta G^\circ = -RT \ln K^\circ \quad (2)$$

where R is the constant $0.001987 \text{ kcal deg}^{-1} \text{ mole}^{-1}$

At 25°C or 298.15°K the relationship is:

$$\log K^\circ = - \left(\frac{\Delta G_{\text{Rx}}^\circ}{1.364} \right) \quad (3)$$

For the reaction $\text{Al(OH)}_3 = \text{Al}^{3+} + 3 \text{OH}^-$ the equilibrium constant can be derived if the free energies of the solid and the solution species are known. The following are taken from Sadiq and Lindsay, 1979.

$$\begin{aligned} \Delta G_{\text{Al(OH)}_3(c)}^\circ &= -276.43 \text{ kcal mole}^{-1} \\ \Delta G_{\text{Al}^{3+}(aq)}^\circ &= -117.33 \text{ kcal mole}^{-1} \\ \Delta G_{\text{OH}^-(aq)}^\circ &= -37.594 \text{ kcal mole}^{-1} \end{aligned}$$

For the reaction ΔG° is:

$$\Delta G_{\text{Rx}}^\circ = [-117.33 + 3(-37.594)] - [-276.43] \quad (4)$$

From (4) and (3) the equilibrium constant is:

$$\log K^\circ = - \frac{46.318}{1.364} = -33.957$$

Note that the stoichiometries of the reactants and products are maintained in the summation process. Also remember that for other units such as kJ mole^{-1} , the constants will change.

Review Questions

1. Why is the ion activity product an important concept with respect to solubility of minerals and compounds?
2. If mineral solubilities are determined by IAP's, what does saturation, supersaturation and undersaturation imply about equilibrium?
3. If sodium chloride dissolves in water to form a saturated solution, does the activity of Na always equal the activity of Cl?
4. How does ionic strength affect the solubility of gypsum if the solid is present? What if the solution is not in contact with a solid phase?
5. The level of soluble Si has important implications for clay mineral stability in soils. Why is silica so important?
6. For the mineral dicalcium phosphate, the IAP is $(Ca)(HPO_4)$. If the value for the IAP was 10^{-6} , and (Ca) was 10^{-3} , what would the total solution P level be at pH 6.7, and 5.78?
7. If Gibbsite $(Al(OH)_3)$ [$K_{sp} = 10^{-33}$] and Varasite $AlPO_4$ [$K_{sp} = 10^{-35}$] were both present as solids in excess, could you predict the level of P? What would you need to know?
8. If a solution of a mineral is saturated, will the concentrations of the ions always be the same? Explain.