

INTRODUCTION

The material in this document has been assembled to assist in instruction of Soil Science 102. The sections consists of notes, explanatory prose, mathematical derivations, tables of data, and graphs or figures intended to supplement and/or expand the reading assignments in the required text, ENVIRONMENTAL SOIL CHEMISTRY by D.L. Sparks. It is intended that some of the material in the following sections will be more fully explained in lecture. Thus it is important that the pages under discussion be brought to lecture. You may want to enter some notes onto the pages under discussion and to use ruled paper for other more formal lecture notes. This document is designed to minimize taking notes during lecture.

The topics are arranged to first study the important chemical aspects of the solid phase, and then to examine and review the chemistry necessary for description of the liquid phase. We will then consider how soil components dissolve in the liquid phase and then examine interactions between liquid and solid phase. These solution solid interactions will consider exchange, adsorption, buffering and the chemistry of acidic and alkaline soil. Finally, at the end of the quarter we will examine Redox relationships in soils.

Soils are dynamic systems subject to changing temperature and moisture regimes. Despite the dynamic nature of soils, insights about soil reactions and processes can be gained by consideration of soils at equilibrium. In this course multi-component simultaneous equilibria is often encountered. An example from introductory chemistry is a system composed of acetic acid (HAc) and water. We know that water always participates in a protolysis or a dissociation reaction described by the chemical notation below.



That can be simplified to:



This relationship states that one mole of water dissociates into one mole of hydronium and one mole of hydroxide. This stoichiometric relationship does not indicate how much of the water dissociates nor the mechanism by which this reaction occurs. The extent of the reaction is given by the equilibrium relationship among water, hydroxide and hydronium:

$$K_w = \frac{(H^+)(OH^-)}{(H_2O)} \quad (2)$$

Remember that the quantities in parentheses are activities and not concentrations. Note also that the convention for pure liquids is the activity of the liquid is 1. Therefore Equation (2) reduces to Equation (2a).

$$K_w = \frac{(H^+)(OH^-)}{(1)} = 1 * 10^{-14} \quad (2a)$$

In water acetic acid dissociates into hydronium and acetate ions as shown below.



The quantitative relationship for acetic acid is given by the dissociation constant

$$K_a = \frac{(H^+)(OAc^-)}{(HOAc)} \quad (4)$$

Note that both the dissociation of water and the dissociation of acetic acid produce hydronium ions. Both reactions are very fast and therefore at virtual equilibrium at all times which in essence is what is meant by simultaneous equilibria.

To calculate a theoretical pH for a "high" total concentration of acetic acid only equation (4) is needed. For a "low" concentration of pure acetic acid added to pure water (CO_2 - free), both equation (2) and (4) are necessary to correctly solve the problem. *[As an exercise, calculate the $pH = -\log(H^+)$ for an aqueous solution containing $10^{-7} M$ acetic acid $[HOAc + OAc^- = 10^{-7} \text{ moles } L^{-1}]$. Assume that activity coefficients = 1, the dissociation constant for acetic acid is $K_a = 10^{-4.5}$, and $K_w = 10^{-14}$. The correct answer is 6.79].* Note that you can calculate a pH using only equation (4) very precisely, however the answer will be wrong because the initial assumptions inherent in using (4) alone are fallacious. Throughout the quarter we will develop graphical and analytical solutions techniques for working with simultaneous equilibria illustrated by the acetate-water example.

We could complicate the system further by bringing the solution to equilibrium with CO_2 in the air and would therefore need additional equilibrium expressions to define the solubility of CO_2 in water and the dissociation of carbonic acid and bicarbonate. The algebra of the solution for such a system becomes more complex; however, the general procedure is the same. The key to the mathematical process is that all the acid-base reactions are simultaneously at equilibrium.

The chemistry of soil water or sediment water systems is the study and quantitative description of simultaneous reactions, many of which are at virtual equilibrium. Computer programs are now available to ease the arithmetic burden of quantitative calculations involving nearly all components of the solid as well as the liquid phases. However, before these programs can be used intelligently, the fundamental behavior of selected system components must be appreciated. This, seemingly, straight-forward exercise of evaluating soil solutions and the solid phase in a quantitative manner is the goal of this course.

We will find that the systems of interest in soils are inherently nonlinear and therefore non-intuitive. Computers and computer programs are very useful in the solution of simultaneous nonlinear problems. To this end, we will examine a number of programs written in BASIC to evaluate these equilibrium systems. There is nothing unique or special about the BASIC language used in these program. Others computer languages may be more efficient or familiar, but we are interested in illustrating the methodology and are not concerned about the specific language used to compute the answers. Spreadsheets can also be a valuable tool for simultaneous equilibria. Remember computers yield precise answers, but these answers are useful only if the fundamental equations and assumptions are correct.

Concepts to remember:

1. Simultaneous equilibria among components is a common assumption in the chemistry of soil-water systems.
2. Simultaneous equations can be solved by algebraic techniques to yield values for unknowns if equations and relationships between equations are known.
3. Chemical compounds and species can be manipulated in algebraic expressions just like any symbolic variable. (some find it easier to manipulate the equations using variables such as x, y and z and then substituting chemical species for the variables)

Things you should know:

1. How to manipulate simultaneous linear equations.
2. Algebraic manipulations of log and exponential expressions.
3. How to evaluate graphical representations of equations i.e. the meaning of slope, intercept, gradient.