

## SOLUTION CHEMISTRY

Soil solutions bath and nourish microbes and roots, provide the medium in which surface and solution reactions occur, impose osmotic stresses on plants and microbes and transport materials through soil. Despite the fact that soil solutions are found in the pore space of soils, these solutions behave in exactly the same manner as any aqueous phase. Therefore, a review and discussion of the fundamental aspects of dissolved ionic species and solutions are necessary to the conduct of nearly every topic we will cover this quarter.

In general, analytical concentrations can not be used for chemical calculations such as solubility. Analytical methods usually determine total elemental concentrations, while the element may occur in solution as several different ionic forms. In addition, the solutions may behave non-ideally. Non-ideal solutions can be "adjusted" to ideal behavior by using activities rather than concentrations.

In introductory chemistry or other courses you were introduced to concepts of concentration and activity. In many of these instances, the activity of solution was equated to concentration. The implicit or explicit assumption of using concentration rather than activity was the dilute nature of the solute where in activity and concentration are nearly equal. Since many soil solutions are not dilute, concentration and activity are not equal and we need to consider methods to calculate the activities of salts and ions.

Fortunately, methods to estimate single ion activity and the activity of solutes are readily available. Activity is the "effective" concentration of an electrolyte or ion. Only the activity of a solute (salt) has thermodynamic meaning and only the activity of a solute can be measured unambiguously; however, we often need to understand the chemical behavior of individual ions. Therefore, we resort to approximations of ion activities. Concentration and activity are related by the activity coefficient through the general relationship (according to G. N. Lewis)

$$a_i = m_i \gamma_i$$

where:  $a_i$  = the activity of species  $i$

$m_i$  = the concentration of species  $i$  in solution (moles/l)

or (moles/kg solvent)

$\gamma_i$  = the activity coefficient of species  $i$

Activity is related to the chemical energy of salts or ions. Since it is very difficult to know the absolute energy of any system, the easier path is to define the energy relative to a known or hypothetical condition. This is similar to referring to elevation in relation to mean sea level. Using this ploy, it is necessary to choose a reference and standard state for the solutions in question. Most often, the convention used for dilute waters is that the activity

coefficient approaches unity as the solution become more dilute and under these conditions, activity is equal to concentration - a convention used in most introductory chemistry courses. Commonly chosen standard states are shown on the next page. Chapter 2 of Pankow (1991) (*Aquatic Chemistry Concepts*) has an excellent discussion of standard and reference states.

### Commonly Chosen Standard States

<u>Type of Substance</u>	<u>Reference State (<math>f=1</math>)</u>	<u>Concentration Unit</u>	<u>Standard State</u>
<b>Solute</b>	Extremely dilute solution	mole fraction (N)	Hypothetical mole fraction of unity
	Extremely dilute solution	mole per kg of solvent (m)	Hypothetical 1 molal
	Extremely dilute solution	moles per liter of solution (M)	Hypothetical 1 molar
<b>Gases</b>	Pure liquid Low Pressure	mole fraction atmospheres	pure liquid Hypothetical 1 atmosphere
<b>Solids</b>	Pure crystalline solid	mole fraction	Pure crystalline solid

Since analytical methods will report either concentration or activity, the most commonly needed quantity is the activity coefficient. In order to apply this simple relationship, one must have some method of estimating or calculating the activity coefficient.

### Calculation of Activity Coefficients

The quantitative relationship between  $\gamma$  and  $\mu$  take several forms. The simplest is the Debye-Hückel "limiting law" (DH) for a salt:

$$-\log \gamma_{\pm} = A z_+ z_- \mu^{0.5}$$

where:  $A = 0.509$  at  $25^\circ\text{C}$

$z$  = charge on the ion

$\mu$  = ionic strength ( $\text{mol L}^{-1}$ )

For a single ion activity coefficient, the form is:

$$-\log \gamma_i = 0.509 z_i^2 \mu^{0.5}$$

The DH "limiting law" expression is useful only in very dilute solutions (ionic strengths  $< 10^{-2.3}$ ) in part because the classical derivation of the expression assumes ions are point charges having no volume.

There are several different methods to calculate ion activities. We will use the Davies equation given below throughout the quarter. It is useful for  $\mu < 10^{-1}$ .

$$-\log g_i = A z_i^2 \left[ \frac{\sqrt{m}}{1 + \sqrt{m}} - 0.3 m \right]$$

The Davies expression contains the empirical correction term ( $-0.3 \mu$  [others have suggested 0.2 (Stumm and Morgan, 1981)]. It is particularly valuable in dealing with solutions of high ionic strength ( $\mu < 0.5 M$ ). Note also, that since there are no ion-specific parameters such as contained in the Extended DH formulation, the Davies equation is a useful expression for computer programs where the activities of several ions are computed.

Other more involved techniques are also available for calculating activity coefficients at very high ionic strengths. The Pitzer approach has been used in sea water and brine solutions and would be appropriate for evaporation ponds. Anderson and Crerar (1993) present a summary of this approach and others.

Inspection of the above equations indicates that these equations are derived for charged species and can not be applied to uncharged complexes or nonelectrolytes. Empirical expressions are available for nonelectrolyte solutions that relate activities to ionic strength. One such expression is given in Bohn *et al.* 1985.

$$\log \gamma = -k_m I$$

where  $k_m$  is the salting coefficient and  $I$  is ionic strength.

Harned and Owen (1943) have tabulated values for some nonelectrolytes. Values range from 0.01 to 0.2 for common nonelectrolytes (Bohn *et al.* 1985). Uncharged ions pairs are often assumed to have an activity coefficient of 1.

Ionic strength has been an important aspect of the techniques for calculation of activity coefficients. Ionic strength ( $\mu$ ) can be thought of as an index of the strength of the electrical field which each ion in solution experiences." It is defined by the deceptively simple expression:  $\mu = 0.5 \sum (m_i z_i^2)$ . The stronger or more intense the electrical field, the less active is each ion in the solution. Qualitatively, each ion thus appears to experience some electrical "drag" or "friction" which lowers its chemical activity. If the solution is very dilute (low concentration of ions) the ions are very far apart and therefore the strength of the electrical field which any one ion "sees" is so small as to be negligible. Under these conditions,  $\gamma = 1$  and  $a = m$ . If the solution contains a high concentration of ions, then  $\gamma < 1$  and  $a < m$ . (N.B. this is true for all ions including those which may be present at trace concentrations; e.g.

Zn<sup>2+</sup> in a mixture of dissolved mineral salts present in the sample at very high concentrations, has a  $\gamma$  with approximately the same numerical value as Mg<sup>2+</sup>. But Mg<sup>2+</sup> may have a concentration 1000 to 10,000 times greater than Zn<sup>2+</sup>.)

Most laboratory analytical methods report total concentrations ( $m_i$ ) of an element. In these cases, we will often need to calculate ion activities. In other cases; e.g. glass pH electrode, or ion-selective electrode, our analytical procedure will report activities and we may wish to know concentrations.

### Computing Ionic Strength and Single Ion Activity

The formula for ionic strength is:

$$\mu = \frac{1}{2} \sum (m_i z_i^2)$$

$I$  or  $\mu$  are often as symbols for ionic strength as well as  $s$  I.S. The expression for ionic strength means that one must know the concentration and the valence or charge of all ions in a solution. One calculates the contribution of each ion by multiplying its concentration by the square of its charge and dividing the result by 2; then doing likewise with the second, third, and successive ions until the numerical contribution of each ion has been calculated. The sum of the contributions is  $\mu$  (ionic strength) for that aqueous solution.

#### Example

A water sample is taken from a lake and analyzed for the concentration of dissolved minerals. Calculate ionic strength and single ion activity coefficients using the Davies expression.

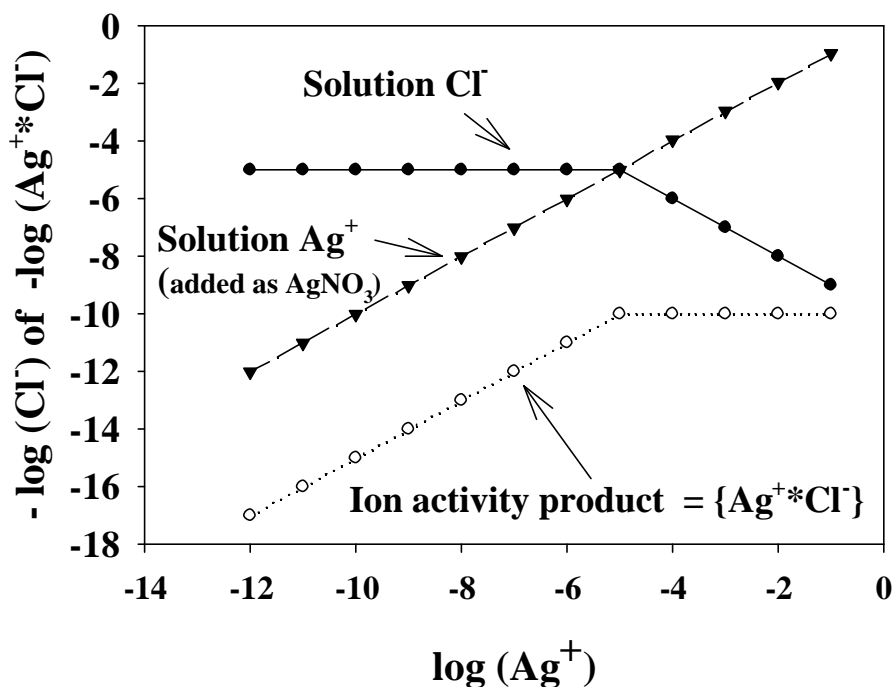
Element	$\frac{m_i}{\text{moles L}^{-1}}$	$\frac{m_i z_i^2}{10^{-3}}$
Na <sup>+</sup>	$3.09 * 10^{-3}$	$3.09 * 10^{-3}$
K <sup>+</sup>	$0.20 * 10^{-3}$	$0.2 * 10^{-3}$
NH <sub>4</sub> <sup>+</sup>	$0.54 * 10^{-3}$	$0.54 * 10^{-3}$
Mg <sup>2+</sup>	$6.04 * 10^{-3}$	$24.16 * 10^{-3}$
Ca <sup>2+</sup>	$10.00 * 10^{-3}$	$40.00 * 10^{-3}$
Mn <sup>2+</sup>	$0.25 * 10^{-3}$	$1.00 * 10^{-3}$
SO <sub>4</sub> <sup>2-</sup>	$2.08 * 10^{-3}$	$8.32 * 10^{-3}$
HCO <sub>3</sub> <sup>-</sup>	$0.22 * 10^{-3}$	$0.22 * 10^{-3}$
NO <sub>3</sub> <sup>-</sup>	$31.43 * 10^{-3}$	$31.43 * 10^{-3}$
Cl <sup>-</sup>	$3.13 * 10^{-3}$	$3.13 * 10^{-3}$
		$\Sigma_i m_i z_i^2 = 112.09 * 10^{-3}$
		$\mu = 0.056$

$$\gamma_{+} = \gamma_{-} = 0.818; \quad \gamma_{2+} = \gamma_{2-} = 0.448; \quad \gamma_{3+} = \gamma_{3-} = 0.164$$

Note that the above assumes that all of the ions are completely dissociated which is technically incorrect because a significant fraction of some of the ions (e.g. Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>) are associated into ion pairs or complexes. Note that whereas H<sup>+</sup> and OH<sup>-</sup> are two of the ions that always exist in aqueous solutions, their concentrations may be so low that they do not contribute significantly to ionic strength as in the above example.

**Ion Activity Product (IAP)** is another important concept in electrolyte solutions. You are probably most familiar with the concept applied to the solubility of sparingly soluble salts. IAP of electrolytes can be calculated even when there is no precipitate involved. Figure 4.1 is an example of applying the ideas of IAP to a solution of NaCl to which  $\text{AgNO}_3$  is added. In this figure, the IAP of AgCl, and the activity of Cl and Ag are plotted in relation to the activity of Ag that is determined by the addition of sufficient  $\text{AgNO}_3$  to give the indicated values of Ag. If AgCl precipitates to lower Ag, then more  $\text{AgNO}_3$  is added until the indicated level of Ag is reached. The graph illustrates several important concepts about solutions and activity products

**Figure 3.1** The Activity of chloride, silver and silver chloride in relation to added  $\text{AgNO}_3$  for a solution of NaCl initially present at 0.01 mM. Values are plotted as logs.



### ION SPECIATION

A second reason that analytical concentration values can not be used directly in calculations is because the element may be distributed among several ionic species including ion pairs, complexes, different protolytic species, chelates or polymeric complexes. Table 3.1 lists several elements and the important species known to exist for these elements. The solubility of many soil components limits their concentration and activity in solutions. Table 3.2 and 3.3 list the solubility constants for several soil components. As we discussed in the solid phase section, we can graph the relationship between solution phase ions and a solid phase. By a similar process, we can graphically represent solution complexes. The Figure 3.2 on page 3.7 is redrawn from Lindsay, (1979), is a two dimensional depiction of Ca complexes in soil solutions.

**Table 3.1. Important and minor dissolved species for a number of important elements in fresh waters.**

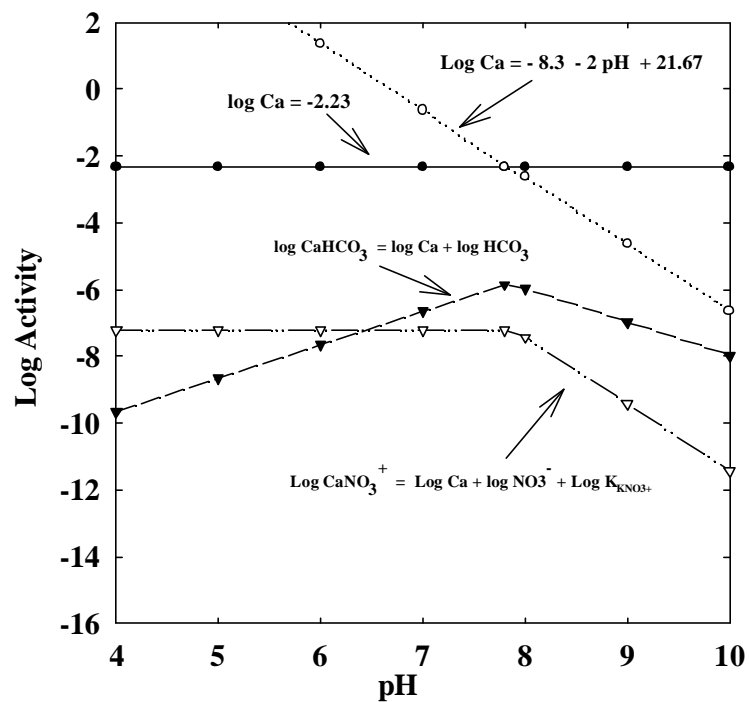
Element	Quantitatively Important Species Known to exist but usually present in minor quantities	
Ca	$\text{Ca}^{2+}$ , $\text{CaSO}_4^0$	$\text{CaCO}_3^0$ , $\text{CaHPO}_4^0$ , $\text{CaH}_2\text{PO}_4^+$
Mg	$\text{Mg}^{2+}$ , $\text{MgSO}_4^0$	$\text{MgCO}_3^0$ , $\text{MgHCO}_3^+$ , $\text{MgHPO}_4^0$
Na	$\text{Na}^+$	$\text{NaHCO}_3^0$ , $\text{NaCO}_3^-$ , $\text{NaSO}_4^-$
K	$\text{K}^+$	$\text{KSO}_4^-$
N	$\text{NH}_4^+$ , $\text{NH}_3^0$	
Mn	$\text{Mn}^{2+}$	$\text{MnSO}_4^0$ , $\text{MnCO}_3^0$
Zn	$\text{Zn}^{2+}$ , $\text{ZnOH}^+$	$\text{ZnSO}_4^0$
Cu	SOC	$\text{Cu}^{2+}$ , $\text{CuOH}^+$ , $\text{CuSO}_4^0$ , $\text{CuCl}^+$
Al	$\text{Al}^{3+}$ , $\text{AlOH}^{2+}$ , $\text{Al(OH)}_2^+$ , $\text{Al(OH)}_3^0$ $\text{Al(OH)}_4^-$ , SOC	
S	$\text{SO}_4^{2-}$ , $\text{CaSO}_4^0$ , $\text{MgSO}_4^0$	$\text{HSO}_4^-$ , $\text{NaSO}_4^-$ , $\text{KSO}_4^-$ , $\text{MnSO}_4^0$ , $\text{FeSO}_4^0$ , $\text{ZnSO}_4^0$ , $\text{CuSO}_4^0$ , $\text{H}_2\text{S}$ , $\text{HS}^-$ , $\text{S}^{2-}$
N	$\text{NO}_3^-$ , $\text{N}_{2(\text{aq})}$	$\text{NO}_2^-$ , $\text{N}_2\text{O}_{(\text{aq})}$ , SOAP
Cl	$\text{Cl}^-$	$\text{CuCl}^+$
P	$\text{H}_2\text{PO}_4^-$ , $\text{HPO}_4^{2-}$ , $\text{MgHPO}_4^0$ , $\text{CaHPO}_4^0$ $\text{CaHPO}_4^+$ , SOAP	$\text{MnHPO}_4^0$ , $\text{AlH}_2\text{PO}_4^{2+}$ , $\text{FeHPO}_4^{2+}$ , $\text{FeHPO}_4^+$
Si	$\text{H}_4\text{SiO}_4$ , $\text{H}_3\text{SiO}_4^-$	
B	$\text{H}_3\text{BO}_3$ , $\text{B(OH)}_4^-$	SOC
C	$\text{CO}_{2(\text{aq})}$ , $\text{H}_2\text{CO}_3$ , $\text{HCO}_3^-$ , $\text{CO}_3^{2-}$	SOAP, $\text{CaCO}_3^0$ , $\text{CaHCO}_3^+$ , $\text{MgCO}_3^0$ , $\text{MgHCO}_3^+$ , $\text{NaHCO}_3^0$ , $\text{NaCO}_3^-$

Note 1: SOC - Soluble organic complex (esp. sugars and organic ligands exposing vicinal hydroxyls and carboxylates.)

Note 2: SOAP - Soluble organic anions and polyanions (e.g. low F.W. carboxylates such as acetate, uronides, phenolates as well as fulvates)

Selected and adapted from L.G. Sillen and A.E. Martell Stability Constants of Metal Ion Complexes Spec. Publ. #17, The Chemical Society, London. 1964.

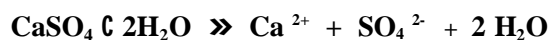
Figure 3.2. Two dimensional graph of Ca solution complexes. Data taken from Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley and Sons. NY. Based on atmospheric levels of  $\text{CO}_2$  and 1 M  $\text{NO}_3^-$  levels.



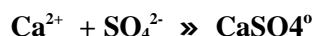
Graphical solutions such as these above present the activity of ions in solution in relation to soil parameters (often pH). The determination of solution concentrations become more involved. In the example below, we will determine the concentration of  $\text{Ca}^{2+}$ ,  $\text{CaSO}_4^0$  and  $\text{Ca}_T$  in a saturated solution of gypsum.

## ITERATIVE CALCULATIONS OF SOLUTION SPECIES

The following is a simple program to calculate the solubility of gypsum in pure CO<sub>2</sub>-free water. It illustrates the strategy of using computers to calculate an equilibrium situation when ionic strength is unknown and determined by the solubility of the solid. In this instance, the dissolution of gypsum increases soluble Ca and SO<sub>4</sub> and increases ionic strength, lowering activities and make an iterative solution necessary. The solubility equation is:



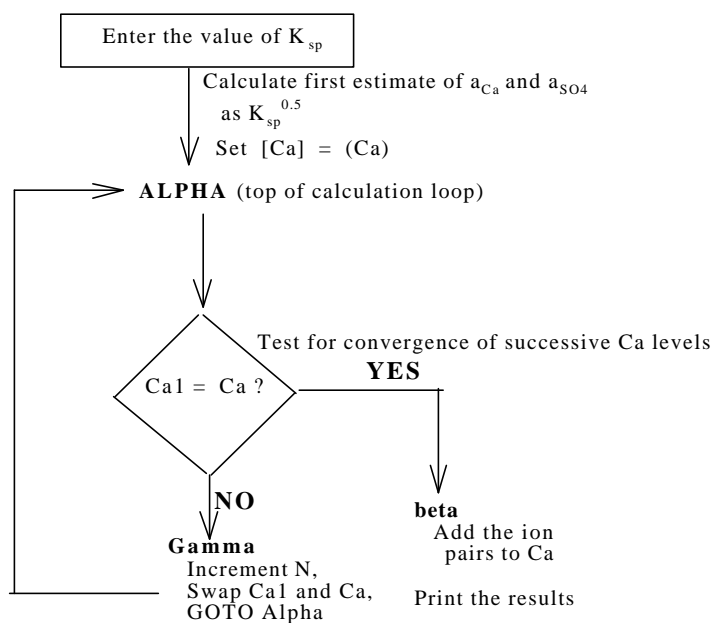
the formation of ion pairs is described by:



**Mass balance:**  $[\text{Ca}]_T = [\text{Ca}^{2+}] + [\text{CaSO}_4^0]$  where  $[\ ] = \text{concentration}$

**Equilibria:**  $[\text{CaSO}_4^0] = K_1^0 g_2^2 [\text{Ca}^{2+}][\text{SO}_4^{2-}]$   
 $K_{sp}^0 = g_2^2 [\text{Ca}^{2+}][\text{SO}_4^{2-}]$

### Strategy for computer program





```

1  REM A simple program to calculate the solubility of gypsum in pure water
2  REM using Ksp,the Davies equation and ionic strength as inputs.
3  REM Property of the Regent of the University of California
4  REM R.J. Zasoski programmer 02-3-92
5  N = 0
6  CLS
7  INPUT " Enter Ksp in ###.## e - y notation  ", Ksp
8  PRINT
9  PRINT 10 REM Calculate the activity of Ca which is also equal to sulfate activity.
11 CaA = Ksp ^ .5
12 PRINT " Calcium activity is = ", CaA
13 Ca = CaA  REM Sets Ca = to calcium activity
14 alpha:  REM Top of computation loop for calculation of ionic strength and Ca activity
15 REM Since SO4=Ca, the value of ionic strength (mu) is 0.5*(Ca*4 + SO4*4) = 4*Ca
16 mu = 4 * Ca
17 musq = mu ^ .5
18 PRINT "mu =", mu
19 REM log g2 = -A* Z^2*((mu^0.5/1+mu^0.5) -0.3*mu)), the Davies equation
20 z = ((musq / (1 + musq)) - .3 * mu)
21 g2 = EXP(-2.3 * .509 * 4 * z)  REM Calculates the value of the divalent activity coefficient
22 PRINT "Gamma 2 is = ", g2
23 Ca1 = CaA / g2  REM calculates calcium concentration from activity and g2.
24 PRINT
25 PRINT "Ca = ", Ca1: PRINT "Ca in ppm = ", Ca1 * 40000 REM Converts moles/L to ppm
26 zz = (Ca1 - Ca) * 40000  REM compares the two estimates of Ca
27 PRINT " zz = ", zz
28 IF zz < .5 THEN GOTO beta ELSE GOTO gamma REM test to see if the two estimates are within 0.5 ppm, if within 0.5 ppm the
program branches to beta, if not branches to gamma.
29 gamma:
30 N = N + 1  REM Increments the counter
31 SWAP Ca1, Ca  REM Replaces the concentration of Ca last estimated with the new estimate
32 GOTO alpha  REM Returns to the top of the computation loop
33 beta:  REM The output
34 REM Add the contribution of ion pairs to total Ca in solution
35 REM The product Ksp* Kion pair = CaSO4 is invariant with Ca aq
36 Kion = 204.17
37 CaT = ((Ksp * Kion) + Ca1
38 Caion = Ksp * Kion
39 PRINT Caion
40 PRINT N, "iterations have been performed to converge within 0.5 ppm"
41 PRINT
42 PRINT
43 PRINT "Ca ion pairs = ", Caion * 1000, "mM/L"
44 PRINT "CaT is = ", CaT * 1000, "mM/L"
45 PRINT "CaT is = ", CaT * 40000, "mg / L"
46 PRINT "Ca2+ is = ", Ca1 * 1000, " mM / L "
47 PRINT "Ca activity is = ", CaA
48 PRINT "the activity coefficient is ", USING "#.###"; g2
49 END

```

### Ca and Mg Speciation in Waters containing Sulfate

The following program and description expands on the gypsum program to presents an algorithm to calculate concentrations of free ions and ion pairs given laboratory data on the composition of a water sample containing Ca, Mg, Na, K HCO<sub>3</sub> and SO<sub>4</sub>.

**Mass balance:**  $[Ca]_T = [Ca^{2+}] + [CaSO_4^0]$  where  $[ ]$  = concentration and  $[ ]_T$  = total analytical concentrations

$$[Mg]_T = [Mg^{2+}] + [MgSO_4^0]$$

$$[SO_4]_T = [SO_4^{2-}] + [CaSO_4^0] + [MgSO_4^0]$$

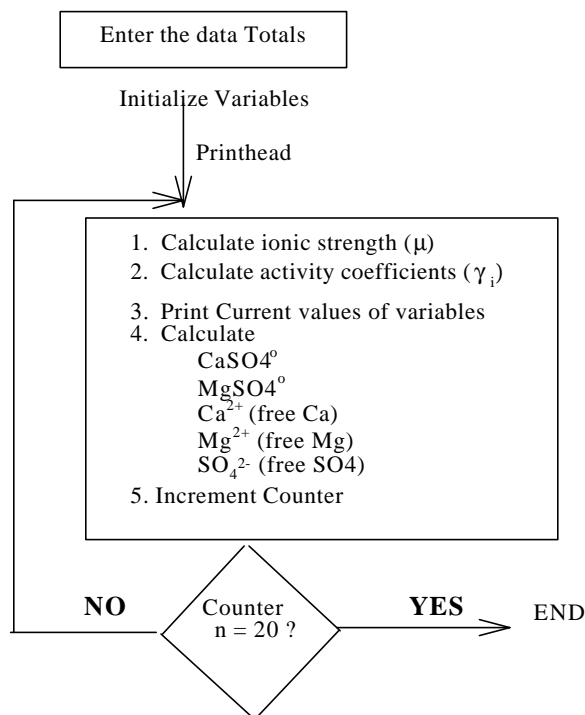
### Equilibria

$$[CaSO_4^0] = \frac{g_2^2 [Ca^{2+}] [SO_4^{2-}]}{K_1}$$

$$[MgSO_4^0] = \frac{g_2^2 [Mg^{2+}] [SO_4^{2-}]}{K_2}$$

Note that the ion pair constants are dissolution constants and not stability constants.

Strategy for computer Program



```
1 REM ** PROGRAM TO CALCULATE FREE ION CONCENTRATIONS OF CALCIUM,**
2 REM ** MAGNESIUM, AND SULFATE FROM ANALYTICAL VALUES IN A WATER
3 REM ** SAMPLE. PROPERTY OF THE REGENTS OF THE UNIVERSITY OF
4 REM ** CALIFORNIA. PROGRAM IS DESIGNED TO ILLUSTRATE THE ITERATIVE
5 REM ** PROCESS TO STUDENTS IN SSC 102. R. G. BURAU. DEPARTMENT OF
6 REM ** LAND, AIR AND WATER RESOURCES. UNIVERSITY OF CALIFORNIA,DAVIS.
7 REM ** February 5, 1984. *****
10 PRINT CHR$(26)
20 DEFDBL A-Y
30 INPUT;"CA TOTAL = ",CAT
40 INPUT;" MG TOTAL = ",MGT
50 INPUT" K = ",K
60 INPUT;"NA = ",NA
70 INPUT;" CL = ",CL
80 INPUT" S04 TOTAL = ",S04T
90 INPUT;"HC03 = ",HC03
100 X3 = 2*CAT+2*MGT+K+NA-(CL+2S04T+HC03)
110 X1 = ABS(X3)
120 K1 = 10^-2.274
130 K2 = 10^-2.253
140 Z = 0
150 CAS04 = 0
160 MGS04 = 0
170 CA = CAT
180 MG = MGT
190 S04 = S04T
200 LPRINT "ENTERED VALUES IN MOL/L ARE: "
210 LPRINT USING "CA = ##### MG = #####NA = ##### K = #####"; CA,MG,NA,K
220 LPRINT USING " CL = ##### S04 = ##### HCO3 = #####"; CL,S04,HC03
230 LPRINT
240 LPRINT "Iteration";TAB(15): I.S.":TAB(25);" CASO4" ; TAB(35)
250 LPRINT " MGS04":TAB(45);" CA"; TAB(55);" MG":TAB(65) " S04"
260 I = 2*(CA+MG+S04)+.5*(NA+K+CL+HC03+X1)
270 G2 = 0.509*2*(SQR(I)/(1+SQR(I))-.3*I)
280 G2 = 10^(-G2)
290 LPRINT USING " ## ###. ##### #. ##### #.##### #.#####";Z,I,CASO4, MGSO4,CA;
300 LPRINT USING "###.##### #.#####"; MG;S04
310 CAS04 = G2*G2*CA*S04/K1
320 MGS04 = G2*G2*MG*S04/K2
330 CA = CAT-CAS04
340 MG = MGT-MGS04
350 S04 = S04T-CAS04-MGS04
360 Z = Z+1
370 IF Z = 20 THEN END ELSE GOTO 260
```

ENTERED VALUES IN MOL/L ARE:

CA =0.020300 MG =0.002620 Na =0.000000 K = 0.000000

CL =0.000000 SO<sub>4</sub> =0.010100 HC03 =0.002000

ITERATION	I.S.	CASO <sub>4</sub>	MGSO <sub>4</sub>	CA	MG	SO <sub>4</sub>
0	0.078860	0.000000	0.000000	0.020300	0.002620	0.010100
1	0.050292	0.006360	0.000782	0.013940	0.001838	0.002958
2	0.071441	0.001648	0.000207	0.018652	0.002413	0.008245
3	0.056184	0.005047	0.000622	0.015253	0.001998	0.004431
4	0.067432	0.002540	0.000317	0.017760	0.002303	0.007243
5	0.059256	0.004362	0.000539	0.015938	0.002081	0.005199
6	0.065266	0.003023	0.000376	0.017277	0.002244	0.006701
7	0.060882	0.004000	0.000408	0.016300	0.002125	0.005605
8	0.064098	0.0032B3	0.000408	0.017017	0.002212	0.006410
9	0.061748	0.003807	0.000471	0.016493	0.002149	0.005822
10	0.063471	0.003423	0.000425	0.016877	0.002195	0.006253
11	0.062211	0.003703	0.000459	0.016597	0.002161	0.005938
12	0.063134	0.003498	0.000434	0.016802	0.002186	0.006168
13	0.062458	0.003648	0.000452	0.016652	0.002168	0.006000
14	0.062953	0.003538	0.000439	0.016762	0.002181	0.006123
15	0.062591	0.003619	0.000449	0.016681	0.002171	0.006033
16	0.062856	0.003560	0.000441	0.016740	0.002179	0.006099
17	0.06266	0.003603	0.000447	0.016697	0.002173	0.006051
18	0.062804	0.003571	0.000443	0.016729	0.002177	0.006086
19	0.062700	0.003594	0.000446	0.016706	0.002174	0.006060

**Table 3.2. REACTIONS OF SELECTED SOIL MINERALS**

Taken from Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley &amp; Sons. N.Y. Pg. 88-89

Reaction No.	Equilibrium Reaction	Log K
<b>Silicates</b>		
1.	$\beta\text{-CaSiO}_3$ (wollastonite) + 2 H <sup>+</sup> + H <sub>2</sub> O = Ca <sup>2+</sup> + H <sub>4</sub> SiO <sub>4</sub> <sup>o</sup>	13.27
2.	CaSiO <sub>3</sub> (pseudowollastonite) + 2 H <sup>+</sup> + H <sub>2</sub> O = Ca <sup>2+</sup> + H <sub>4</sub> SiO <sub>4</sub> <sup>o</sup>	14.23
3.	$\beta\text{-Ca}_2\text{SiO}_4$ (larnite) + 4 H <sup>+</sup> = 2 Ca <sup>2+</sup> + H <sub>4</sub> SiO <sub>4</sub> <sup>o</sup>	39.62
4.	?-Ca <sub>2</sub> SiO <sub>4</sub> (Ca olivine) + 4 H <sup>+</sup> = 2 Ca <sup>2+</sup> + H <sub>4</sub> SiO <sub>4</sub> <sup>o</sup>	37.82
<b>Aluminosilicates</b>		
5.	CaAl <sub>2</sub> SiO <sub>6</sub> (pyroxene) + 8 H <sup>+</sup> = Ca <sup>2+</sup> + 2 Al <sup>3+</sup> + H <sub>4</sub> SiO <sub>4</sub> <sup>o</sup> + 2 H <sub>2</sub> O	35.25
6.	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> (Ca-glass) + 8H <sup>+</sup> = Ca <sup>2+</sup> + 2 Al <sup>3+</sup> + 2 H <sub>4</sub> SiO <sub>4</sub> <sup>o</sup>	33.91
7.	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> (hexagonal anorthite) + 8 H <sup>+</sup> = Ca <sup>2+</sup> + 2 Al <sup>3+</sup> + 2 H <sub>4</sub> SiO <sub>4</sub> <sup>o</sup>	26.10
8.	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> (anorthite) + 8 H <sup>+</sup> = Ca <sup>2+</sup> + 2 Al <sup>3+</sup> + 2 H <sub>4</sub> SiO <sub>4</sub> <sup>o</sup>	23.33
9.	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> • 2 H <sub>2</sub> O (lawsonite) + 8 H <sup>+</sup> = Ca <sup>2+</sup> + 2 Al <sup>3+</sup> + 2 H <sub>4</sub> SiO <sub>4</sub> <sup>o</sup> + 2 H <sub>2</sub> O	17.54
10.	CaAl <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> • 2 H <sub>2</sub> O (wairakite) + 8 H <sup>+</sup> = Ca <sup>2+</sup> + 2 Al <sup>3+</sup> + 2 H <sub>4</sub> SiO <sub>4</sub> <sup>o</sup>	16.05
11.	Ca <sub>2</sub> Al <sub>4</sub> Si <sub>8</sub> O <sub>24</sub> • 7 H <sub>2</sub> O (leonhardite) + 16 H <sup>+</sup> + H <sub>2</sub> O = 2 Ca <sup>2+</sup> + 4 Al <sup>3+</sup> + 8 H <sub>4</sub> SiO <sub>4</sub> <sup>o</sup>	17.29
12.	CaMg(SiO <sub>3</sub> ) <sub>2</sub> (diopside) + 4 H <sup>+</sup> + 2 H <sub>2</sub> O = Ca <sup>2+</sup> + Mg <sup>2+</sup> + 2 H <sub>4</sub> SiO <sub>4</sub> <sup>o</sup>	21.16
<b>Carbonates</b>		
13.	CaCO <sub>3</sub> (calcite) + 2 H <sup>+</sup> = Ca <sup>2+</sup> + CO <sub>2(g)</sub> + H <sub>2</sub> O	9.74
14.	CaCO <sub>3</sub> (aragonite) + 2 H <sup>+</sup> = Ca <sup>2+</sup> + CO <sub>2(g)</sub> + H <sub>2</sub> O	9.97
15.	CaCO <sub>3</sub> • 6 H <sub>2</sub> O (ikaite) + 2 H <sup>+</sup> = Ca <sup>2+</sup> + CO <sub>2(g)</sub> + 7 H <sub>2</sub> O	11.7
16.	CaMg(CO <sub>3</sub> ) <sub>2</sub> (dolomite) + 4 H <sup>+</sup> = Ca <sup>2+</sup> + Mg <sup>2+</sup> + 2 CO <sub>2(g)</sub> + 2 H <sub>2</sub> O	18.46
<b>Soil, Oxides, Hydroxides, Ferrites</b>		
17.	Soil-Ca = Ca <sup>2+</sup>	-2.50*
18.	CaO (lime) + 2 H <sup>+</sup> = Ca <sup>2+</sup> + H <sub>2</sub> O	32.95
19.	Ca(OH) <sub>2</sub> (portlandite) + 2 H <sup>+</sup> = Ca <sup>2+</sup> + 2H <sub>2</sub> O	22.80
20.	CaFe <sub>2</sub> O <sub>4(c)</sub> + 8 H <sup>+</sup> = Ca <sup>2+</sup> + 2 Fe <sup>3+</sup> + 4 H <sub>2</sub> O	21.42
<b>Sulfates</b>		
21.	CaSO <sub>4</sub> (insoluble) = Ca <sup>2+</sup> + SO <sub>4</sub> <sup>2-</sup>	-4.41
22.	α-CaSO <sub>4</sub> (soluble) = Ca <sup>2+</sup> + SO <sub>4</sub> <sup>2-</sup>	-2.45
23.	β-CaSO <sub>4</sub> (soluble) = Ca <sup>2+</sup> + SO <sub>4</sub> <sup>2-</sup>	-1.75
24.	CaSO <sub>4</sub> • 2 H <sub>2</sub> O (gypsum) = Ca <sup>2+</sup> + SO <sub>4</sub> <sup>2-</sup> + 2 H <sub>2</sub> O	-4.64
<b>Fluorides</b>		
25.	CaF <sub>2</sub> (fluorite) = Ca <sup>2+</sup> + 2F <sup>-</sup>	-10.41

<b>Solution Complexes</b>		
26.	$\text{Ca}^{2+} + \text{Cl}^- = \text{CaCl}^+$	-1.00
27.	$\text{Ca}^{2+} + 2 \text{Cl}^- = \text{CaCl}_2^0$	0.00
28.	$\text{Ca}^{2+} + \text{CO}_{2(\text{g})} + \text{H}_2\text{O} = \text{CaHCO}_3^+ + \text{H}^+$	-6.70
29.	$\text{Ca}^{2+} + \text{CO}_{2(\text{g})} + \text{H}_2\text{O} = \text{CaCO}_3^0 + 2 \text{H}^+$	-15.01
30.	$\text{Ca}^{2+} + \text{NO}_3^- = \text{CaNO}_3^+$	-4.80
31.	$\text{Ca}^{2+} + 2 \text{NO}_3^- = \text{Ca}(\text{NO}_3)_2^0$	-4.50
32.	$\text{Ca}^{2+} + \text{H}_2\text{O} = \text{CaOH}^+ + \text{H}^+$	-12.70
33.	$\text{Ca}^{2+} + 2 \text{H}_2\text{O} = \text{Ca}(\text{OH})_2^0 + 2 \text{H}^+$	-27.99
34.	$\text{Ca}^{2+} + \text{H}_2\text{PO}_4^- = \text{CaH}_2\text{PO}_4$	1.40
35.	$\text{Ca}^{2+} + \text{H}_2\text{PO}_4^- = \text{CaHPO}_4^0 + \text{H}^+$	-4.46
36.	$\text{Ca}^{2+} + \text{H}_2\text{PO}_4^- = \text{CaPO}_4^- + 2 \text{H}^+$	-13.09
37.	$\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4^0$	2.31

**Table 3.3. Selected Solubility Constants for Solid Phases that may Affect the Composition of Fresh Waters**

<u>Crystal Modification</u>	<u>Dissolution Reaction</u>	<u>pK = -log K</u>
gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	4.60
calcite	$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$	8.35
amorphous active {(Fe(OH) <sub>3</sub> }	$\text{Fe}(\text{OH})_3 = \text{Fe}^{3+} + 3 \text{OH}^-$	38.7*
ferric hydroxide		
gibbsite	$\text{Al}(\text{OH})_3 = \text{Al}^{3+} + 3 \text{OH}^-$	33.8
bayerite	$\text{Al}(\text{OH})_3 = \text{Al}^{3+} + 3 \text{OH}^-$	33.0
variscite	$\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4 = \text{Al}^{3+} + 2 \text{OH}^- + \text{H}_2\text{PO}_4^-$	30.5
strengite	$\text{Fe}(\text{OH})_2\text{H}_2\text{PO}_4 = \text{Fe}^{3+} + 2 \text{OH}^- + \text{H}_2\text{PO}_4^-$	35

\* Determined in a system containing 3 M NaClO<sub>4</sub>

## **KINETIC CONSIDERATIONS**

There are a number of reasons that chemical reactions in soils do not attain equilibria, or the equilibria (pseudoequilibria) established does not conform to the predictions based on pure solutions and solids. We will not discuss this, however it is important to recognize the limitations imposed by a "classical" thermodynamic approach.

### **Additional Reading:**

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## Review Questions

1. Analytical concentrations often can not be used to compute or model soil chemical reactions. Why?
2. What is the distinction between concentration and activity ?
3. How can the activity of an electrolyte measured ? How can the activity of ions be measured?
4. How is the activity of an electrolyte and ion calculated ?
5. What is the IAP ? What is saturation ? Supersaturation? Undersaturation
6. Why can EC be related to ionic strength ?
7. What is  $pAg^+$  ,  $pCl^-$  ,  $pH$  ?
8. What is the Davies Equation ?
9. For the reaction of excess  $CaSO_4 \cdot 2H_2O$  dissolving in water show that the ion pair is always constant.
10. To depict the activity of  $CaCl^+$  graphically what must you know?
11. What is the graphical form of the following equation  $Ag^+ \cdot Cl^- = K_{sp}$  in linear and log forms?
12. A solution of NaBr was added to a beaker to give a  $Br^-$  concentration of  $1 \cdot 10^{-7}$  moles/L. This solution has an initial  $Ag^+$  level of  $1 \cdot 10^{-15}$  moles/L. The solution is titrated with  $AgNO_3$  until the  $Ag^+$  level is  $1 \cdot 10^{-1}$  moles/L. In relation to  $Ag^+$  level, how does  $IAP_{AgBr}$  ,and the activity of  $Br^-$  change?

## TERMS

common ion effect	$K^c$ , $K^o$ , $K_{sp}$	ionic strength	undersaturation
ion pair	complex	activity	IAP
saturation	supersaturation	stability diagrams	