CARBONATE EQUILIBRIA

Carbonates are arguably the most important dissolved component of soil solutions and in alkaline soils this statement is even less disputable. Implicit in this statement is the relationship among dissolved carbonate species whether or not they are in equilibrium with solid phase metal carbonates. The simplest example of carbonates is the control which dissolved carbon dioxide has on water pH and buffering. In this section of the course we will consider the effect of carbon dioxide on water pH, the influence of solid phase calcium carbonate on solution composition and the implications of these reactions.

Several systems including carbon dioxide, solution and solid phase carbonates can be envisioned. Some of these include (after Garrels and Christ, 1967).

1. The solution pH of water in equilibrium with carbon dioxide and essentially devoid of other controlling species.
2. The reaction of calcium carbonate saturated solutions with free access to carbon dioxide. In essence this is the equilibrium of lime with air or soil air. Also referred to as an open system with solid phase present. This case is of considerable interest as it represents the relationship of dilute natural waters in contact with the atmosphere and system control only by the carbonate equilibria.
3. The reactions of calcium carbonate with water where the gas phase is restricted or negligible. This condition is not common, but in situations were the equilibrium system has little head space and the mixing of air is restricted the attendant pH and slow rate of return to equilibrium is of interest. This is the famous "Turner Effect". Such as system is also referred to as a closed system since mass is not transferred or exchanged with the surroundings.
4. Equilibrium in systems with a fixed quantity of added alkalinity such as the addition of strong base to a system open to the atmosphere.

Other cases can be considered, however these serve to illustrate the great utility of being able to understand the equilbrium behavior of carbonate species in soils and sediments.

CASE 1 CO_2 - H_2O open system

Aqueous carbon dioxide reacts to form carbonic acid via the following reaction:

$$CO_{2\,(aq)} + H_2O \rightarrow H_2CO_3$$

$$\frac{H_2CO_3}{CO_{2\,(aq)}} = 10^{-2.8} = 0.00159$$

The hydration of carbon dioxide is slow to attain equilibrium below pH 8 in pure systems. However, above pH 11, the hydration reaction is relatively rapid as carbon dioxide reacts directly with hydroxide to form bicarbonate.

$$CO_{2\,(aq)} + OH^- = HCO_3^- \qquad (1)$$

In biological systems the hydration of carbon dioxide is catalyzed by carbonic anhydrase a Zn-containing enzyme. Only a small portion of the aqueous carbon dioxide exists as carbonic acid. However, in most $H_2CO_3^*$ (as defined below) is used to represent solution carbonates.

$$H_2CO_3^* = H_2CO_3 + CO_{2(aq)} \qquad (2)$$

Where $H_2CO_3^*$ is the total dissolved cabon including aqueous carbon dioxide.

Carbonic acid dissociates into bicarbonate and carbonate according to the following equations:

$$\frac{(H^+)\,(HCO_3^-)}{(H_2CO_3)} = K^o_{H_2CO_3} = 10^{-6.4} \qquad (3)$$

where $H_2CO_3 = H_2CO_3 + CO_{2\,(aq)} = H_2CO_3^*$

Note that $K^o_{H2CO3} = 2*10^{-4}$ or pK = 3.69 if corrected for $CO_{2(aq)}$

$$\frac{(H^+)\ (CO_3^{2-})}{(HCO_3^-)} = K^o_{HCO_3^-} = 10^{-10.3} \tag{4}$$

As for every aqueous reaction the acid base relationship between the proton and hydroxide is an important relationship.

$$\frac{(H^+)\ (OH^-)}{(H_2O)} = K^o_W = 10^{-14} \tag{5}$$

Starting with the electrical neutrality expression:

$$[H^+] = [OH^-] + [HCO_3^-] + 2\ [CO_3^{2-}] \tag{6}$$

The system is manipulated to collect terms in the variables of interest - hydrogen ion concentration and carbon dioxide partial pressure. Note that the electrical neutrality expression is defined in terms of concentrations (mol/L). Therefore, in order to utilize values from the thermodynamic equilibrium expressions, the conditional equilibrium constants must be used which relate concentrations rather than activities to the ionic distributions at equilibrium.

Defining OH^- *in terms of* H^+ *yields :*

$$[OH^-] = \frac{K^c_W}{[H^+]} \tag{7}$$

Solving for HCO_3^- *gives :*

$$[HCO_3^-] = \frac{K^c_{H_2CO_3}\ [H_2CO_3]}{[H^+]} \tag{8}$$

Finding carbonate via bicarbonate:

$$[CO_3^{2-}] = \frac{K^c_{HCO_3^-}\ [HCO_3^-]}{[H^+]} \tag{9}$$

Substituting for HCO_3^-:
$$[CO_3^{2-}] = \frac{K^c_{H_2CO_3}\, K^c_{HCO_3^-}\, [H_2CO_3]}{[H^+]^2} \qquad (10)$$

The rewritten electrical neutrality expression in terms of H^+ and H_2CO_3 is:

$$[H^+] = \left(\frac{K^c_W}{[H^+]}\right) + \left(\frac{K^c_{H_2CO_3}\,[H_2CO_3]}{[H^+]}\right) + 2\left(\frac{K^c_{H_2CO_3}\, K^c_{HCO_3^-}\,[H_2CO_3]}{[H^+]^2}\right) \qquad (11)$$

Rearranging, multiplying by $(H^+)^2$ and substituting $k_H * P_{CO2}$ for H_2CO_3 yields:

$$[H^+]^3 - K^c_W\,[H^+] - K^c_{H_2CO_3}\,[H^+]\,k_H P_{CO_2} - 2\,K^c_{H_2CO_3}\,K^c_{HCO_3^-}\,k_H P_{CO_2} = 0$$

$$(12)$$

$$[H^+]^3 - [H^+]\left(K^c_w + K^c_{H_2CO_3}\,k_H P_{CO_2}\right) - 2\,K^c_{H_2CO_3}\,K^c_{HCO_3^-}\,k_H P_{CO_2} = 0$$

We are left with a polynomial equation in $[H^+]$. In this formulation the only variables are (H^+) and P_{CO2}. If a known and constant value for the partial pressure of carbon dioxide is inserted into the above equation, (H^+) can be found by a variety of numerical techniques.

Henry's Law Constant for this reaction is strongly influenced by temperature and slightly affected by ionic strength.

Salt Level	**k_H@ 298K^o**	**Log k_K**
0.2 M NaCl	0.0328	-1.48
0.5 M NaCl	0.0304	-1.57
1.0 M NaCl	0.0273	-1.56

Temp ^{o}K	**k_H @ 0.2 *M* NaCl**	**Log k_H @ 0.2 *M* NaCl**
273 K^o	0.073	-1.13
278 K^o	0.061	-1.21
283 K^o	0.051	-1.29
288 K^o	0.043	-1.36
293 K^o	0.037	-1.47
298 K^o	0.033	-1.48
308 K^o	0.026	-1.58

Dissolved carbon is distributed among three species H_2CO_3, HCO_3 and CO_3 as a function of pH. In soil systems where there may be an external (to the carbonate system) control on pH it would be handy to know the distribution of the carbonate species given pH. This distribution of carbonate species can be derived from the Henderson-Hasslebach relationship knowing pH and pK's. A slightly different approach is shown next.

Assume : C_T = the sum of all carbonate species concentration
activity coefficients are neglected or equal to one.

define z as: $z = (H^+)^2 + (H^+) K_{H2CO3} + K_{H2CO3} K_{HCO3}$ or more generally as:

$z = (H^+)^2 + (H^+) K_1 + K_1 K_2$ where K_1 and K_2 are the first and second dissociation constants for the acid.

then:

$$\frac{[\ H_2CO_3\ ]}{C_T} = \frac{[\ H^+\ ]^2}{Z} \qquad (13)$$

$$\frac{[HCO_3^-]}{C_T} = \frac{[H^+]K_1}{Z} \qquad (14)$$

$$\frac{[H_2CO_3]}{C_T} = \frac{K_1 K_2}{Z} \qquad (15)$$

Figure 5.1. The distribution of carbonate species as a fraction of total dissolved carbonate in relation to solution pH.

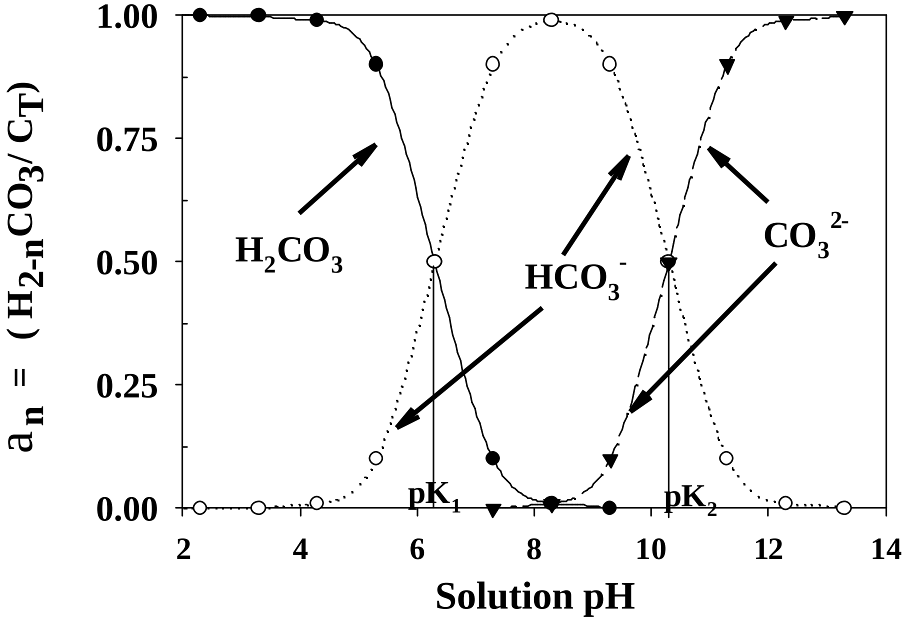


Figure 5.2. The activity of carbonate species in relation to pH for a carbon dioxide level of $10^{-3.5}$ atmospheres.

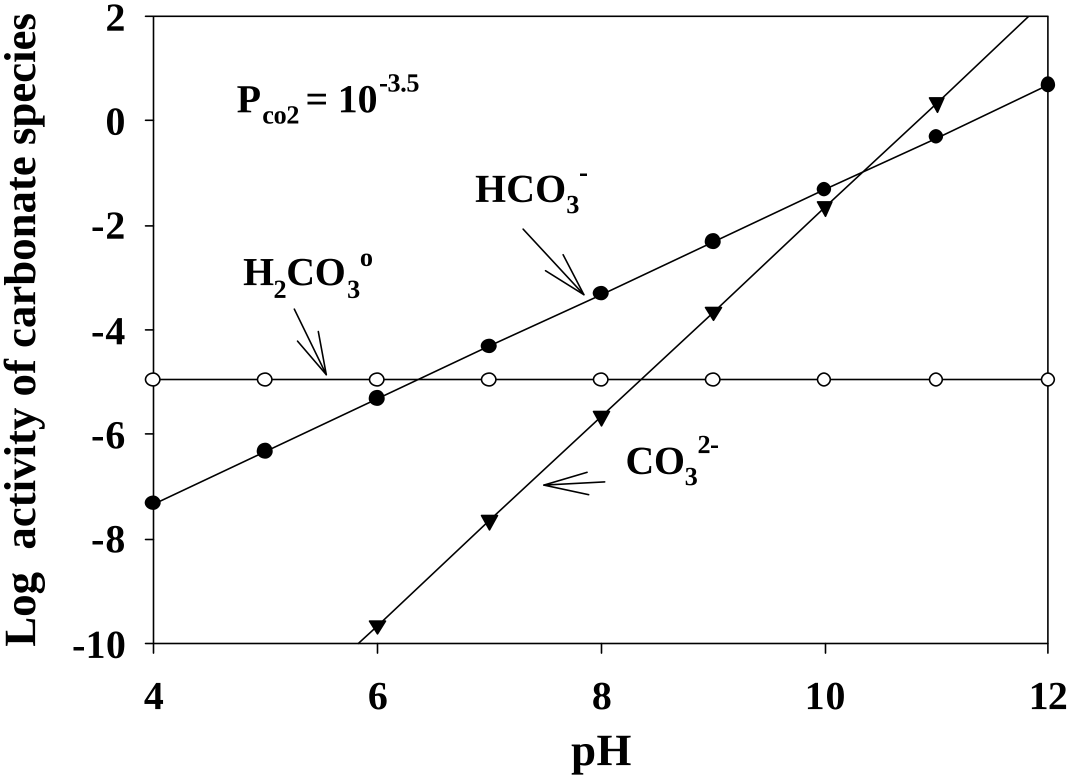
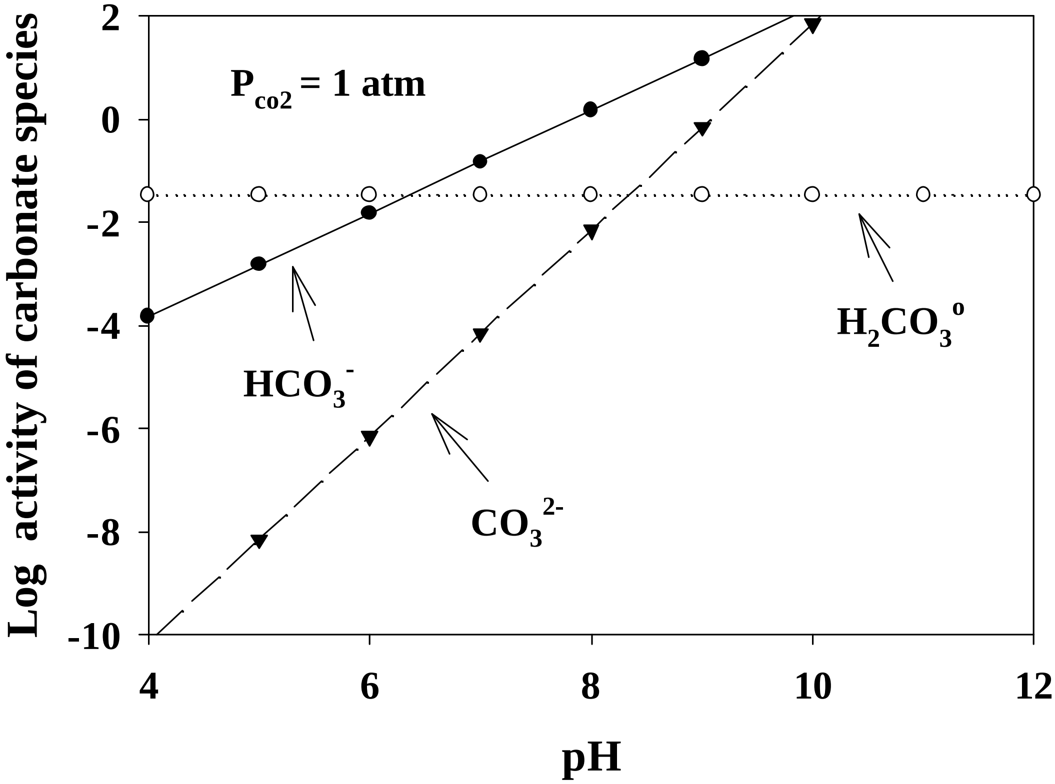


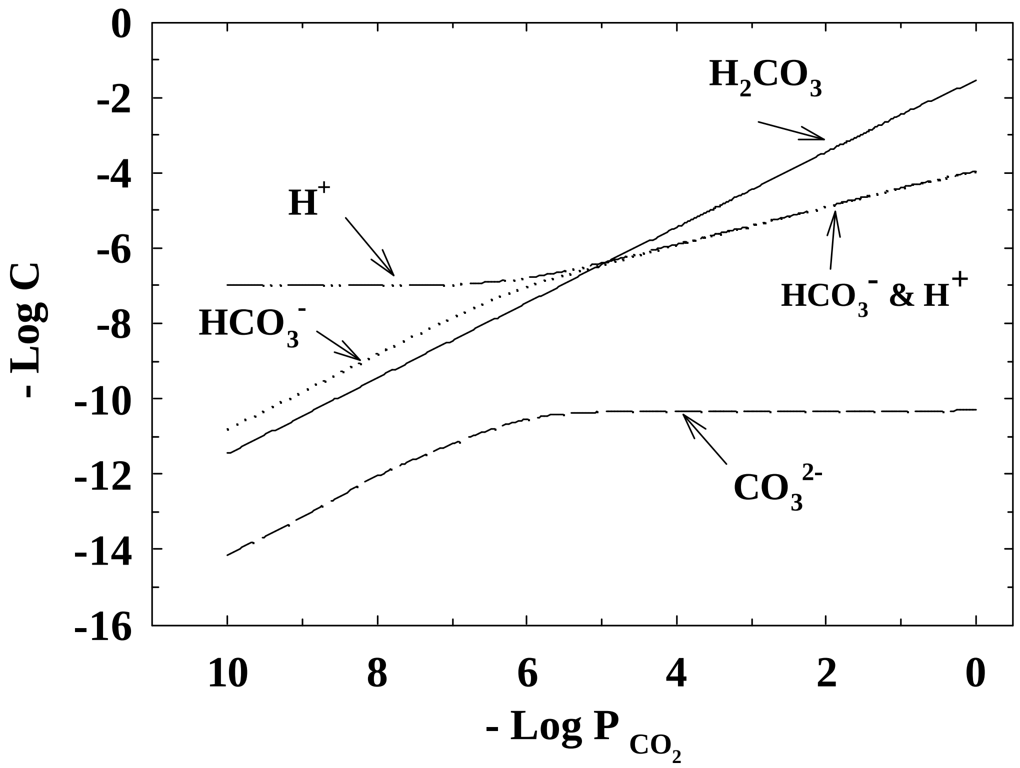
Figure 5.3 . ***The activity of carbonate species in relation to pH for a carbon dioxide level of 1 atmosphere.***



Equilibrium Reactions in the CO_2-H_2O system.

Reaction No.	Equilibrium Reaction	Log K°
1.	$CO_{2(g)} + H_2O \rightleftharpoons H_2CO_3^o$	- 1.46
2.	$H_2CO_3^o \rightleftharpoons H^+ + HCO_3^-$	- 6.36
3.	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	- 10.33
4.	$CO_{2(g)} + H_2O \rightleftharpoons H^+ + HCO_3^-$	- 7.82
5.	$CO_{2(g)} + H_2O \rightleftharpoons 2 H^+ + CO_3^{2-}$	- 18.15

Figure 5.4 Effect of carbon dioxide partial pressure on the solution concentration of carbonate species in the CO_2*-water system.*



ALKALINITY

Examination of Figure 5.4 indicates that as the carbon dioxide partial pressure goes to zero, the solution pH approaches 7 and increasing pressures of carbon dioxide cause the system to be acidic. Therefore, in the CO_2-water system there is never a net excess of base. The system can neutralize added base, but can not neutralize added acid. Another way of saying the same thing is to state that the system do not contain any alkalinity. Alkalinity is an important concept in solution chemistry and relates to the acid neutralization capacity of solutions. The definition of alkalinity for the CO_2-water system is:

$$Alkalinity = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+] \qquad (16)$$

In the CO_2 -water system the electrical neutrality condition for the system is:

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \qquad (17)$$

Substituting the electrical neutrality equation into the alkalinity definition :

$$Alkalinity\ =\ [OH^-]+[HCO_3^-]+2\,[CO_3^{2-}]-[OH^-]-[HCO_3^-]-2\,[CO_3^{2-}] \qquad (18)$$

Therefore, there is no alkalinity in a CO_2-water system, unless other sources of base are added.

Case 2. $CaCO_3$ -CO_2-H_2O system

Calcium carbonate in water with a fixed partial pressure of carbon dioxide.

For the case of a fixed partial pressure of carbon dioxide and calcium carbonate dissolved in the aqueous phase one more equation is need to describe the system. This is the solubility product of calcium carbonate:

$$\frac{(Ca^{2+})(CO_3^{2-})}{(CaCO_3)} = K^o_{CaCO_3} \qquad (19)$$

The electrical neutrality expression for this case is:

$$2\,[Ca^{2+}] + [H^+] = [OH^-] + [HCO_3^-] + 2\,[CO_3^{2-}] \qquad (20)$$

Substituting to produce an equation in H^+ and H_2CO_3 results in the following:

$$[Ca^{2+}] = \frac{K^c_{CaCO_3}}{[CO_3^{2-}]} \qquad (21)$$

As in the previous case:

$$[Ca^{2+}] = \frac{K^c_{CaCO_3}}{\left(\dfrac{K^c_{H_2CO_3}\ K^c_{HCO_3^-}[H_2CO_3]}{[H^+]^2}\right)} \qquad (22)$$

$$[HCO_3^-] = \frac{K^c_{H_2CO_3}[H_2CO_3]}{[H^+]} \qquad (23)$$

$$[CO_3^{2-}] = \frac{K^c_{H_2CO_3}K^c_{HCO_3^-}[H_2CO_3]}{[H^+]^2} \qquad (24)$$

$$[OH^-] = \frac{K^c_W}{[H^+]} \qquad (25)$$

These equations yield an expression in [H_2CO_3] and [H^+] which are can be solved for [H^+] at a given partial pressure of carbon. Knowing [H^+] and P_{CO2} , Ca^{2+}, HCO_3^- and CO_3^{2-} can be found.

Substituting into the electrical neutrality expression yields:

$$[H^+] + 2\left[\frac{K^c_{CaCO_3}}{\left(\dfrac{K^c_{H_2CO_3}\ K^c_{HCO_3^-}\ [H_2CO_3]}{[H^+]^2}\right)}\right] = \frac{K^c_W}{[H^+]} + \frac{K^c_{H_2CO_3}\ [H_2CO_3]}{[H^+]} + \tag{26}$$

$$2\left[\frac{K^c_{H_2CO_3}\ K^c_{HCO_3^-}\ [H_2CO_3]}{[H^+]^2}\right]$$

Replacing [H_2CO_3] with k_H*P_{CO2} gives:

$$[H^+] + 2\left[\frac{K^c_{CaCO_3}}{\left(\dfrac{K^c_{H_2CO_3}\ K^c_{HCO_3^-}\ k_H\ P_{CO_2}}{[H^+]^2}\right)}\right] = \frac{K^c_W}{[H^+]} + \frac{K^c_{H_2CO_3}\ k_H\ P_{CO_2}}{[H^+]} \tag{27}$$

$$+\ 2\left(\frac{K^c_{H_2CO_3}\ K^c_{HCO_3^-}\ k_H\ P_{CO_2}}{[H^+]^2}\right)$$

Rearranging and multiplying by $[H^+]^2$ gives:

$$[H^+]^3 + 2\left(\frac{K_{CaCO_3^c}\ [H^+]^4}{K^c_{H_2CO_3}\ K^c_{HCO_3^-}\ k_H\ P_{CO_2}}\right) - K^c_W\ [H^+] - K^c_{H_2CO_3}\ k_H P_{CO_2}\ [H^+] \tag{28}$$

$$-\ 2\left(K^c_{H_2CO_3}\ K^c_{HCO_3^-}\ k_H\ P_{CO_2}\right) = 0$$

This is a fourth power polynomial in (H^+) which can be solved by trial and error, graphical methods or numerical techniques.

Figure 5.5.   Soluble Ca derived from calcite, gypsum or Portlandite in relation to solution pH. A line depicting soil Ca at an arbitrary value of 3 mMol/l is include, along with the solubility of Ca from gypsum.

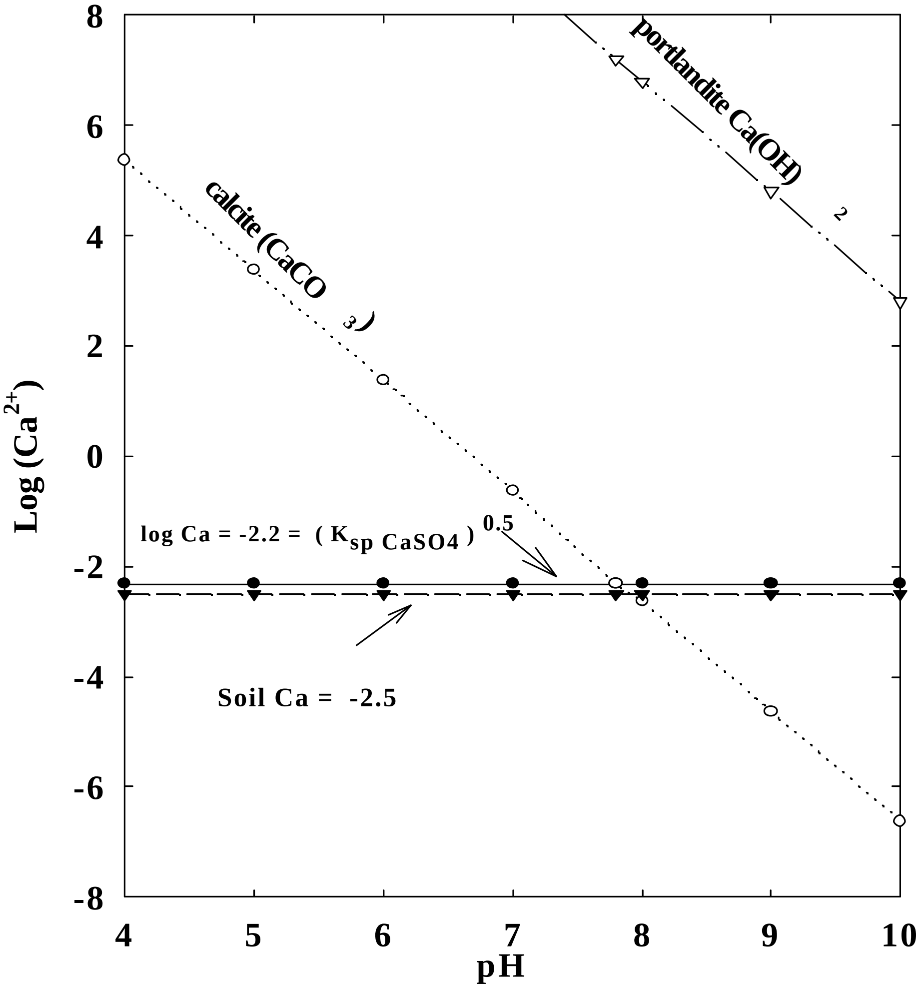


Figure 5.6. Solution concentrations of Ca and carbonate species derived from calcite in relation to the partial pressure of carbon dioxide.

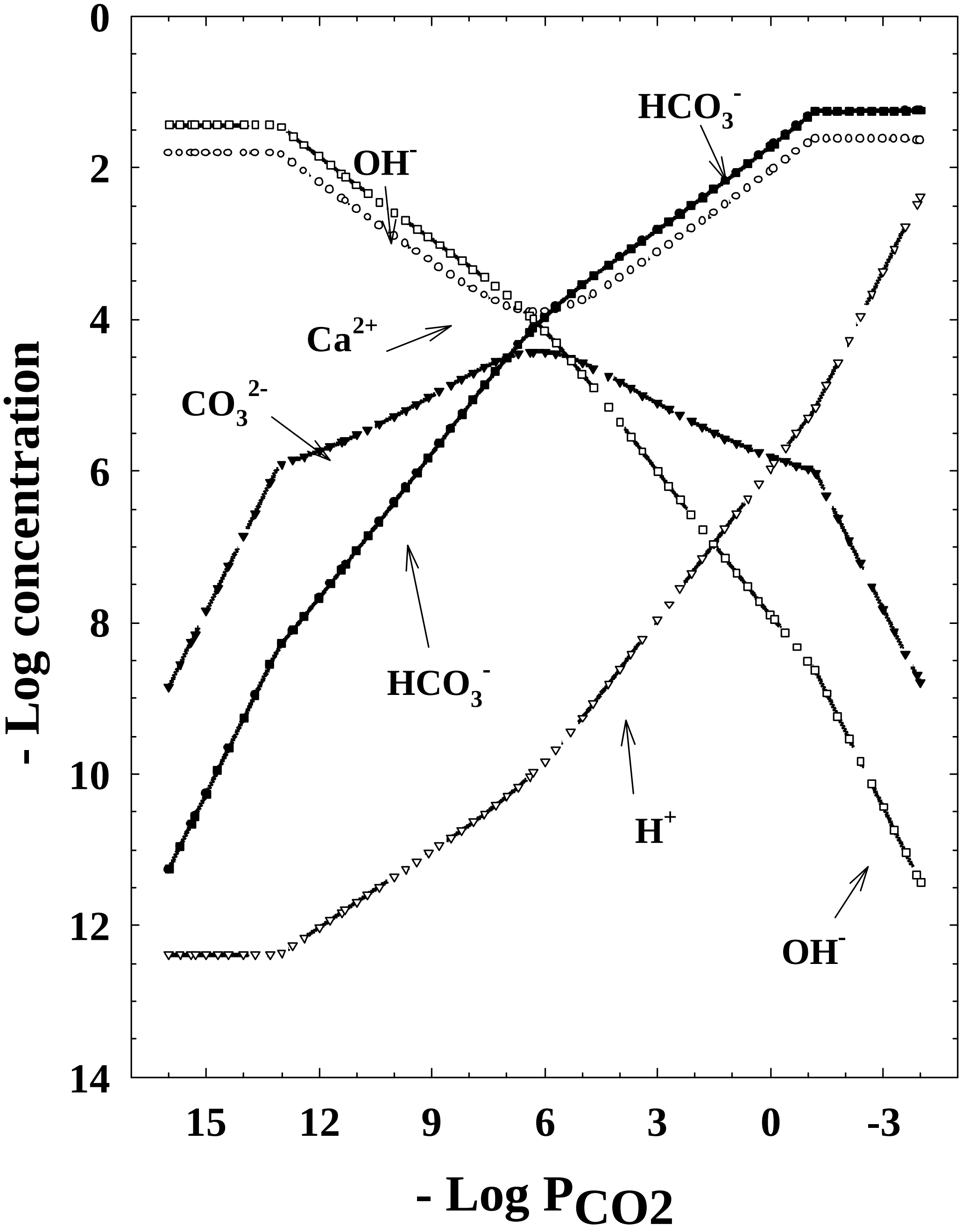
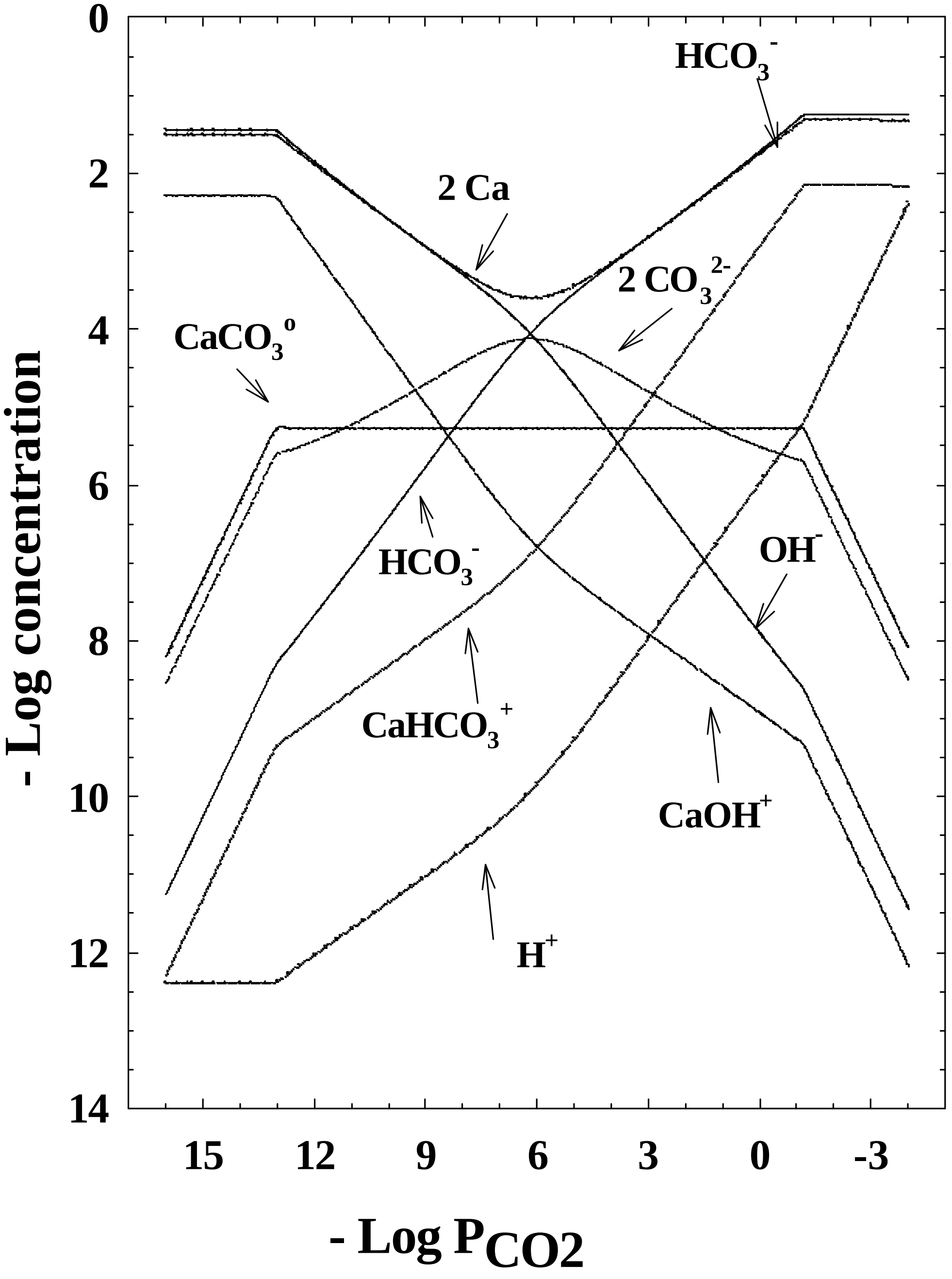


Figure 5.7 Solution concentrations of Ca and carbonate species derived from calcite in relation to the partial pressure of carbon dioxide including ion pairs and complexes. .



CASE 3 Calcite in water without carbon dioxide additions

In the case where access to carbon dioxide is restricted and there is little or no transfer of gases into or out of the solution, the pH can exceed the equilibrium pH of 8.3 for an air-water-calcium carbonate system. This is the case of solid phase carbonate in a closed system and corresponds to dissolving pure calcium carbonate in a gas free solution with no head space. A practical example might include irrigation water entering a dry soil containing carbonates.

In this instance, the total carbonate species are fixed by the solubility of the calcite and do not depend on the partial pressure of the air as in the previous case. Since all of the carbonate species are derived from dissolution of calcite:

$$[Ca^{2+}] = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \qquad (29)$$

Furthermore, the only charged species in solution can be Ca^{2+}, H^+, HCO_3^-, CO_3^{2-} and OH^- which yields the electrical neutrality expression for this system.

$$2\,[Ca^{2+}] + [H^+] = [OH^-] + [HCO_3^-] + 2\,[CO_3^{2-}] \qquad (30)$$

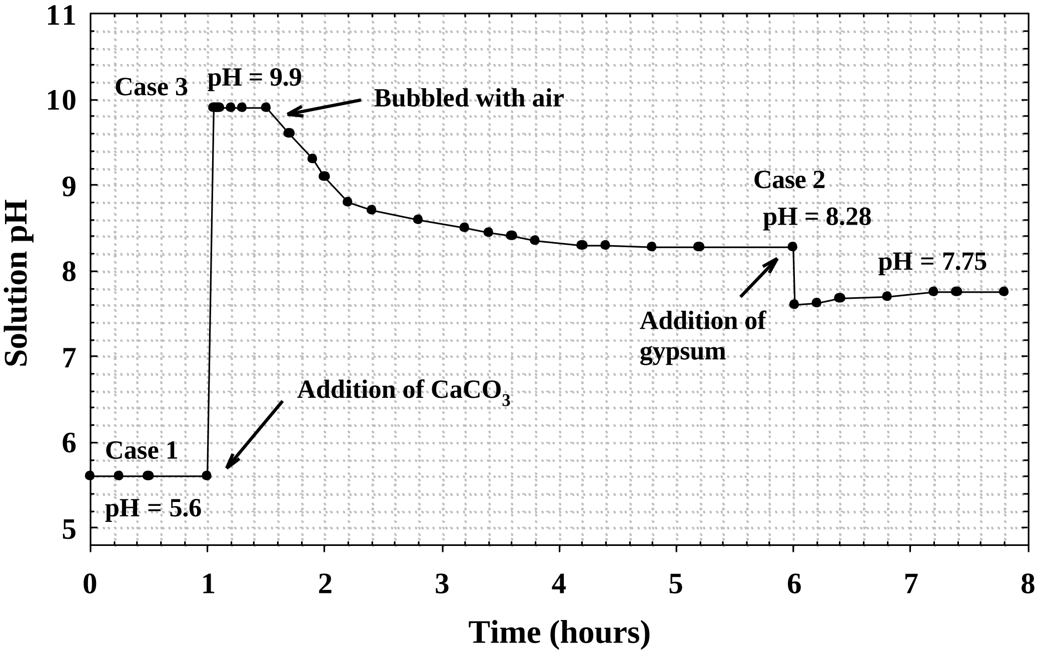
Solution of this case follows on those already presented. In Case 3 carbon dioxide (an acid) is not allowed to enter the system and the final pH of the solution is nearly 10. The alkalinity is generated by the hydrolysis of the carbonate ion. If the carbonate is more soluble, there is more carbonate ion and solution pH reaches a higher value. The reactions generating the high pH are shown below.

$$CaCO_{3(C)} \leftrightarrow Ca^{2+} + CO_3^{2-} \qquad (31)$$

$$CO_3^{2-} + HOH \leftrightarrow HCO_3^- + OH^- \qquad (32)$$

Figure 5.8 is a graph of the changes in pH generated when pure water is bubbled with carbon dioxide (Case 1) followed by the addition of calcium carbonate to reach a pH of 9.9 (Case 3). After the solution reaches the high pH associated with Case 3. As carbon dioxide is bubbled into the solution, CO_2 reacts with to form HCO_3^- and the solution pH returns to 8.3 or Case 2. When OH^- is present, it can react with CO_2 to form HCO_3.

Figure 5.8. Changes in solution pH in relation to experimental manipulation of the carbon dioxide-water and carbon-dioxide-calcium oxide system.



Case 4. The addition of NaOH to water open to the atmosphere.

Case 4 is a situation where all of the added salt is soluble and the initial alkalinity is due to the addition of OH^- in direct relation to the concentration of added NaOH. As in Case 3, CO_2 reacts with OH to form HCO_3^- and over time NaOH becomes $NaHCO_3$. Alkalinity in this case will be equal to the OH added to the system. This is the reason that strong bases are not used as primary standards for acid-base titrations, and a good reason to protect solutions of strong base from contact with the atmosphere. Ascarite is a good adsorbant of carbon dioxide and is often used as a trap for carbon dioxide on bottles of NaOH.

The electrical neutrality expression for Case 4 is:

$$[H^+] \;+\; [Na^+] \;=\; [OH^-] \;+\; [HCO_3^-] \;+\; 2\,[CO_3^{2-}] \qquad (33)$$

If Pco_2 is fixed at atmospheric values, then a set of simultaneous equations can be solved. The concentrations found for this case are presented in Table 5.1.

Table 5.1 is a summary of the various cases we examine in this section on carbonate chemistry and alkalinity. Note that even thought the pH is higher in Case 3 than in Case 2, the alkalinity is higher in Case 2. It is also interesting that the alkalinity in Case 4 is much higher than in either Case 2 or 3. The NaOH with an initial pH of nearly 13 has been titrated by the acid carbon dioxide to a pH of 9.77.

Table 5.1 Solution concentration and properties for Cases 1,2, 3 and 4.

	Case 1	Case 2	Case 3	Case 4
pH	5.666*	8.318	9.944	9.767
P_{CO2}(atm)	3.0E-4	3.0E-4	6.31E-7	3.0E-4
H_2CO_3	1.04E-5	1.04E-5	2.19E-8	1.04E-5
HCO_3^-	2.16E-6	9.87E-4	8.59E-5	3.48E-2
CO_3^{2-}	4.70E-11	1.10E-5	3.79E-5	2.00E-2
Ca^{2+}		5.03E-4	1.24E-4	
$CaOH^+$		1.83E-8	2.02E-7	
$CaHCO_3^+$		5.50E-6	1.28E-7	
$CaCO_3^o$		5.37E-6	5.37E-6	
Na^+				8.69E-2
$NaHCO_3^o$				1.04E-3
$NaCO_3^-$				1.20E-2
C_T	1.26E-5	1.02E-3	1.29E-4	6.79E-2
Ca_T		5.14E-4	1.29E-4	
Alkalinity	0	1.03E-3	2.59E-4	0.100
I.S.	2.16E-6	0.00153	0.00041	0.1009
$(_1$	0.998	0.957	0.977	0.781
$(_2$	0.993	0.840	0.912	0.372

Concentrations are given in mol L_1.,
Case 1 is water in equilibrium with standard air.
Case 2 is water saturated with $CaCO_3$ in equilibrium with standard air.
Case 3 is a closed aqueous system saturated with $CaCO_3$.,
Case 4 is 0.1 *M* NaOH brought to equilibrium with standard air.,
I.S. is ionic strength
*Note: you can calculate pH more precisely than it can be measured.

CARBONATE SUMMARY

It is instructive to note several features of the carbon dioxide-water and carbon dioxide-water- calcium oxide system.

1. Since the electrical neutrality expression and mass balance equations are specified in terms of concentrations and the acid dissociation and solubility expressions are defined in terms of concentrations via conditional equilibrium expressions, the solutions presented here are general but relay on appropriate methods to determine ion activities. For the limited solubility of the calcite systems and the low ionic strength of the carbon dioxide water system, the assumption of unit activity coefficients is reasonable. However, in many waters and soil solutions there are indifferent electrolytes that do not participate in the reactions, but contribute to ionic strength.

2. It should be evident that solving even these simplified equations is laborious and the general solution that iterates to determine the correct ionic strength is a monumental undertaking with out the aid of computers. However, there are a few assumptions that can ease the labor. In the last cases presented, the final pH is alkaline and the contribution of H^+ to the electrical neutrality expression is negligible. Similarly, the contribution of H_2CO_3 to the total carbonate species is also very small and can be ignored with little loss in accuracy.

3. The final pH in the closed system depends on the solubility of the solid phase. For more soluble carbonates, solution alkalinity will be much greater than in the calcite case.

This section has emphasized:

1. Simultaneous equilibria for quantitative description of system behavior.

    a. Note that the "Lindsay" graphical technique is easy to apply because it generally only considers a limited or specialized case and it often makes drastic assumptions in order to develop a linear (log-log) relationship. But it is useful as a **rough**, quick and dirty guide to behavior.

    b. The quantitative approach requires a mathematical development including mass or charge balance plus the judicious selection of the applicable equilibrium (thermodynamic) expressions, iterative calculation of ionic strength and activity corrections. It is practicable only with a programmable calculator or a computer.

c. The quantitative approach can be extended from a specific case to a series of calculations covering a range of a key variable so that the results can be graphed. This is exemplified by the graphs on pages 5-12 and 5-13. This general type of graph is often called a "Bjerrum" graph. Note how much more information is given by the "Bjerrum" graph on pages 5-12 and 5-13 than by the Lindsay graph on page 5-11. Also note that the same equilibrium expressions (top of page 7-8) are used in constructing both graphs.

2. Calcium ion always acts as an acid.

3. Role of atmospheric (gas phase) CO_2 in affecting solution phase composition.

a. In soils and sediments, partial pressure of CO_2 can range widely; e.g., from 10^{-6} to one atmosphere. Note: At depth in water, hydrostatic pressure increases the total pressure on any gas phase (bubble).

b. Sampling of soil water by vacuum or suction techniques can drastically affect equilibria in the water being extracted.

c. Bioaquatic effects: Diurnal pH shifts. Lakes, marshes, estuaries, and rice paddies may show a maximum pH during the day ($pH \leq 9.5$) but a pH minimum during the night ($pH \geq 7$). The phenomenon is due to extraction of CO_2 **from** the alkalinity in the water during the day to carry on photosynthesis (algae, other phytoplankta). (Note that such organisms are carrying on respiration during the day but CO_2 uptake for photosynthesis is > > than CO_2 release from respiration. During the night, the dominant process is release of CO_2 to the water by respiration. ***Nota Bene***: During the day, pH cannot go over 7 unless the water contains alkalinity.

The following program was written to calculate the distribution of carbonate species in the carbon dioxide water system in relation to the partial pressure of carbon dioxide in the atmosphere. The results are tabulated and the data also is shown in Figure 5.4 on page 5-8.

```
The Property of the Regents of the University of California            February 13, 1989

100 REM Case specific program to calculate pH and all carbonate species          SSC110
110 REM in pure water as a function of partial pressure of C02              R.G. Burau
120 CLS
130 DEFDBL A-W
140 DIFF  =  .00001#
150 DEF FNDEL(A,B) = ABS(A-B)* 2/ ABS(A+B)
160 OPEN "O",1,"B:SSPCO2"
170 K1 =  10^-6.35 : K2 = 10^-10.33 : KW = .00000000000001# : KH = 10^-1.46
180 RESTORE 190
190 DATA 1,1,lD-7,0,0,0,0
200 READ G11, G21, H1, OH1, HCO31, C031, IS1
210 FOR ZPCO2=-10 TO 0 STEP .1
220 PCO2 = 10^ ZC02
230 REM ..........Top of NEWTON-RAPHSON
240 KWC = KW/G11/G11
Z50 K1C = K1/G11/G11
260 K2C = K2/G21
270 F = H1 ^3 - (KWC + K1C*KH*PCO2)*H1 - 2 K1C *K2C*KH*PCO2
280 IF F = 0 THEN 570
290 F1 = 3*H1 ^2 - KWC - K1C*KH*PCO2
300 IF F1 <> 0 THEN 330
310 N1 = 1.0001*H1
320 GOTO 270
330 H2 = H1-F/F1
340 HCO32 = K1C*KH*PCO2/H2
350 C032 = K2C* HCO32/H2
360 OH2 = KWC/H2
370 IS2 = 2*C032 + (HCO32 + OH2 + H2)/2
380 G = (SQ (lS2)/(l+SQ(lS2)))-.3*IS2
39O G12 = 10^-(.5*G)
400 G22 = 10^-(2*G)
410 SWAP H2,H1 : SWAP HCO32,HC031 : SWAP C032,C031 : SWAP OH2,OH1
420 SWAP IS2,IS1 : SWAP G12,G11 : SWAP G22,G21
430 DEL = FNDEL(H1,H2)
440 IF DEL > DIFF THEN 230
450 DEL = FNDEL(HCO32,HCO31)
460 IF DEL > DIFF THEN 230
470 DEL = FNDEL(CO32,CO31)
480 IF DEL > DIFF THEN 230
490 DEL = FNDEL(OH2,OH1)
500 IF DEL > DIFF THEN 230
510 DEL = FNDEL(lS2,IS1)
520 IF DEL > DIFF THEN 230
530 DEL = FNDEL(G12,G11)
540 IF DEL > DIFF THEN 230
550 DEL = FNDEL(G22,G21)
560 IF DEL > DIFF THEN 230
570 ZPH = LOG(H1*Gll)/LOG(10)
580 ZH2CO3 = LOG(KH*PCO2)/LOG(10)
590 ZHCO3 = L0G(HCO31)/LOG(10)
600 ZC03 = LOG(CO31)/LOG(IO)
610 ZIS = IS1
620 ZG1 = Gll
630 PRINT  -ZPCO2, -ZPH, -ZHCO3, ZIS, ZG1
640 PRINT  #1, ZPCO2; ZPH; ZH2CO3; ZHCO3; ZC03; ZIS; ZG1
650 NEXT  ZPCO2
660 CLOSE : END
```

CARBONATE SPECIES AND pH AS A FUNCTION OF P_{CO2}

Log concentration

P_{CO2}	H^+	H_2C0_3	HCO_3^-	CO_3^{2-}	IS	G1
- 10	- 6.999	- 11.46	- 10.81	- 14.139	1.0004 E-07	0.9996
- 9.5	- 6.555	- 10.96	- 10.31	- 13.640	1.0006 E-07	0.9996
- 9.1	- 6.999	- 10.56	- 9.910	- 13.240	1.0009 E-07	0.9996
- 8.5	- 6.998	- 9.996	- 9.311	- 12.641	1.0028 E-07	0.9996
- 8.0	- 6.996	- 9.456	- 8.813	- 12.146	1.0081 E-07	0.9996
- 7.5	- 6.989	- 8.956	- 8.320	- 11.660	1.0246 E-07	0.9996
- 7.0	- 6.968	- 8.460	- 7.841	- 11.202	1.0752 E-07	0.9996
- 6.5	- 6.913	- 7.960	- 7.396	- 10.812	1.2214 E-07	0.9996
- 6.0	- 6.796	- 7.460	- 7.013	- 10.546	1.5978 E-07	0.9995
- 5.5	- 6.614	- 6.960	- 6.695	- 10.410	2.4307 E-07	0.9994
- 5.0	- 6.391	- 6.460	- 6.418	- 10.356	4.0644 E-07	0.9992
- 4.5	- 6.150	- 5.960	- 6.159	- 10.337	7.0773 E-07	0.9990
- 4.0	- 5.903	- 5.460	- 5.906	- 10.331	1.2502 E-06	0.9987
- 3.5	- 5.654	- 4.960	- 5.654	- 10.328	2.2192 E-06	0.9983
- 3.0	- 5.404	- 4.460	- 5.404	- 10.326	3.9458 E-06	0.9977
- 2.5	- 5.154	- 3.960	- 5.154	- 10.325	7.0205 E-06	0.9970
- 2.0	- 4.904	- 3.460	- 4.903	- 10.323	1.2456 E-05	0.9960
- 1.5	- 4.654	- 2.960	- 4.652	- 10.321	2.2251 E-05	0.9946
- 1.0	- 4.404	- 2.460	- 4.402	- 10.318	3.9639 E-05	0.9928
- 0.5	- 4.154	- 1.960	- 4.151	- 10.313	7.0658 E-05	0.9905
- 0.1	- 3.954	- 1.560	- 3.950	- 10.309	1.1226 E-04	0.9880

R.G. Burau SSC102 February 13, 198

COMPUTER SOLUTION OF SIMULTANEOUS EQUILIBRIA

To illustrate the creation of a polynomial expression from a series of simultaneous equations which can then be solved by a Newton-Raphson (NR) or other numerical process, calculate equilibrium values for the system $CaCO_3$ - $CaSO_4$ - H_2O- Air.

All the appropriate simultaneous equilibria are represented by:

$$K_{1c} = [\,Ca^{2+}\,][\,CO_3^{2-}\,] = \frac{4.47 * 10^{-9}}{g_2^2} \qquad (1)$$

$$K_{2c} = [\,Ca^{2+}\,][\,SO_4^{2-}\,] = \frac{2.51 * 10^{-5}}{g_2^2} \qquad (2)$$

$$K_{3c} = \frac{[\,H^+\,]\,[\,HCO_3^-\,]}{[\,H_2CO_3\,]} = \frac{4.45 * 10^{-7}}{g_1^2} \qquad (3)$$

$$K_{4c} = \frac{[\,H^+\,]\,[\,CO_3^{2-}\,]}{[\,HCO_3^-\,]} = \frac{4.69 * 10^{-11}}{g_2} \qquad (4)$$

$$K_{5c} = \frac{[Ca^{2+}][SO_4^{2-}]}{[CaSO_4^o]} = 5.32 * 10^{-5} \qquad (5)$$

$$(H_2CO_3) = k_H P_{CO_2} = 1.05 * 10^{-5} \qquad (6)$$

$$K_{wc} = [H^+][OH^-] = \frac{10^{-14}}{g_1^2} \qquad (7)$$

The electrical neutrality expression is:

$$2[Ca^{2+}] + [H^+] = 2[CO_3^{2-}] + 2[SO_4^{2-}] + [HCO_3^-] + [OH^-] \qquad (8)$$

Note that this last expression can be modified by elimination and substitution using (1) to (7) as necessary into a polynomial in 1 variable having exponents; 0, 1, 2, . . . m. Since we are interested in pH, an expression in $[H^+]$ is convenient.

Substituting from above in (8):

$$\frac{2K_{1c}[H^+]^2}{K_{4c}K_{3c}k_H P_{CO_2}} + [H^+] = \frac{2K_{2c}K_{3c}K_{4c}k_H P_{CO_2}}{K_{1c}[H^+]^2} + \frac{2K_{4c}K_{3c}k_H P_{CO_2}}{[H^+]^2} + \frac{K_{3c}k_H P_{CO_2}}{[H^+]} + \frac{K_{wc}}{[H^+]} \qquad (9)$$

Multiplying both sides by $[H^+]^2$ and rearranging:

$$\frac{2K_{1c}[H^+]^4}{K_{4c}K_{3c}k_H P_{CO_2}} + [H^+]^3 - \left(k_H P_{CO_2}K_{3c} + K_{wc}\right)[H^+] - \left(\frac{2K_{2c}K_{3c}K_{4c}k_H P_{CO_2}}{K_{1c}} + 2K_{4c}K_{3c}K_H P_{CO_2}\right) = 0 \quad (1)$$

Evaluating the coefficients leads to the desired polynomial:

$$4.08*10^{13}[H^+]^4 + [H^+]^3 - 4.68*10^{-12}[H^+] - 2.46*10^{-18} = 0 = f$$

Note that previous expressions all used conditional equilibrium constants (K's). In a real computer program, the ionic strength is estimated and from this estimate the activity coefficients are calculated allowing for an initial estimate of K_c. Subsequently, in each iteration of the program new ionic strengths, K_c's, activity coefficients and concentrations are estimated. These values are used in the Newton-Raphson process (NR) which converges on the correct value for $[H^+]$. In the first iteration all activity coefficients are set to 1. An initial guess for $[H^+]$ must be entered for the NR procedure. Using $[H^+]_i = 10^{-8.5}$ for the initial guess, and finding the first derivative of the polynomial (f'), which is:

$$\mathbf{1.63 * 10^{14}[H^+]^3 + 3[H^+]^2 - 4.68 * 10^{-12} = f'}$$

If the current estimate of $[H^+]$ is $[H^+]_i$, then the next estimate by the NR technique is $[H^+]_{i+1}$ and the estimate is given by:

$$\mathbf{[H^+]_{i+1} = [H^+]_i - (f / f')}$$

the new value of $[\text{H}^+]$, $[\text{H}^+]_{i+1}$ is then used to calculate values for **all** other constituents starting with equation (3) to calculate $[\text{HCO}_3^-]$ then proceeding to (4) to calculate $[\text{CO}_3^{2-}]$, . . . and ending with (2) to calculate $[\text{SO}_4^{2-}]$. These values are used to calculate a new estimate of ionic strength that is then processed through the various equations to calculate new values of the activity coefficients using the Davies equation or other expressions. These "new" activity coefficients are then used to find new conditional K's and these in turn are used to find new values for the coefficients in (10).

Computer output during a NEWTON-RAPHSON solution of polynomial for the system gypsum-calcite-water-air using pH = log $[\text{H}^+]$ = 8.5 as the initial estimate of pH.

```
                                             pH
    Iteration                                8.5000
    Iteration          1                     5.2832
    Iteration          2                     5.4083
    Iteration          3                     5.5334
    Iteration          4                     5.6585
    Iteration          5                     5.7837
    Iteration          6                     5.9088
    Iteration          7                     6.0339
    Iteration          8                     6.1590
    Iteration          9                     6.2841
    Iteration          10                    6.4092
    Iteration          11                    6.5344
    Iteration          12                    6.6595
    Iteration          13                    6.7846
    Iteration          14                    6.9097
    Iteration          15                    7.0348
    Iteration          16                    7.1597
    Iteration          17                    7.2844
    Iteration          18                    7.4083
    Iteration          19                    7.5294
    Iteration          20                    7.6427
    Iteration          21                    7.7354
    Iteration          22                    7.7881
    Iteration          23                    7.8011
    Iteration          24                    7.8017
    Iteration          25                    7.8017
    Iteration          26                    7.8017
                       27
```

Graphical solutions to the carbonate system can be very helpful to the understanding of carbonate chemistry. They can be rendered in either the log activity form we are familiar with or in the log concentration form that follows from the equations presented above. Both endeavors rely on the availability of solubility constants, dissociation constants and ion pair formation constants for the appropriate species. The following table taken from Lindsay (1979) presents the important constants.

Reaction No.	Equilibrium Reaction	log K^o
	Carbonates	
13.	$CaCO_3$ (calcite) + 2 H^+ = Ca^{2+} + $CO_{2(g)}$ + H_2O	9.74
14.	$CaCO_3$ (aragonite) + 2 H+ = Ca^{2+} + $CO_{2(g)}$ + H_2O	9.97
15.	$CaCO_3$**?** 6 H_2O (ikaite) + 2 H^+ = Ca^{2+} + $CO_{2(g)}$ + 7 H_2O	11.7
16.	$CaMg(CO_3)_2$ (dolomite) + 4 H^+ = Ca^{2+} + Mg^{2+} + 2 $CO_{2(g)}$ + 2 H_2O	18.46
	Soil, Oxides, Hydroxides, Ferrites	
17.	Soil-Ca = Ca^{2+}	-2.50*
18.	CaO (lime) + 2 H^+ =Ca^{2+} + H_2O	32.95
19.	$Ca(OH)_2$ (portlandite) + 2 H^+ =Ca^{2+} + 2H_2O	22.80
20.	$CaFe_2O_{4(c)}$ + 8 H^+ = Ca^{2+} + 2 Fe^{3+} + 4 H_2O	21.42
	Sulfates	
21.	$CaSO_4$ (insoluble) = Ca^{2+} + SO_4^{2-}	-4.41
22.	a-$CaSO_4$ (soluble) = Ca^{2+} + SO_4^{2-}	-2.45
23.	ß-$CaSO_4$ (soluble) = Ca^{2+} + SO_4^{2-}	-1.75
24.	$CaSO_4$**?** 2 H_20 (gypsum) = Ca^{2+} + SO_4^{2-} + 2 H_2O	-4.64

All of the above equations were taken from Lindsay 1979. *Chemical Equilibria in Soils,* Chapter 7. John Wiley and Sons, New York.

Newton-Raphson Method of find Solutions for polynomials.

The solution of polynomial equations relies on being able to find the point where $f(x) = 0$. Normally the procedure would be to factor the equation into a series of terms such as

(x-a) (x-b) = 0

Then by inspection, one can set x = a or b and the roots of the equation are found. In the case of a quardatic equation, this solution is:

$$\left\{x-\left(\frac{-b-\sqrt{b^2-4ac}}{2a}\right)\right\} \qquad \left\{x-\left(\frac{-b+\sqrt{b^2-4ac}}{2a}\right)\right\}$$

Multiplied out this is the more familiar $\left(ax^2+bx+c=0\right)$

While there are exact solutions for quadratic and cubic functions, the general polynomial

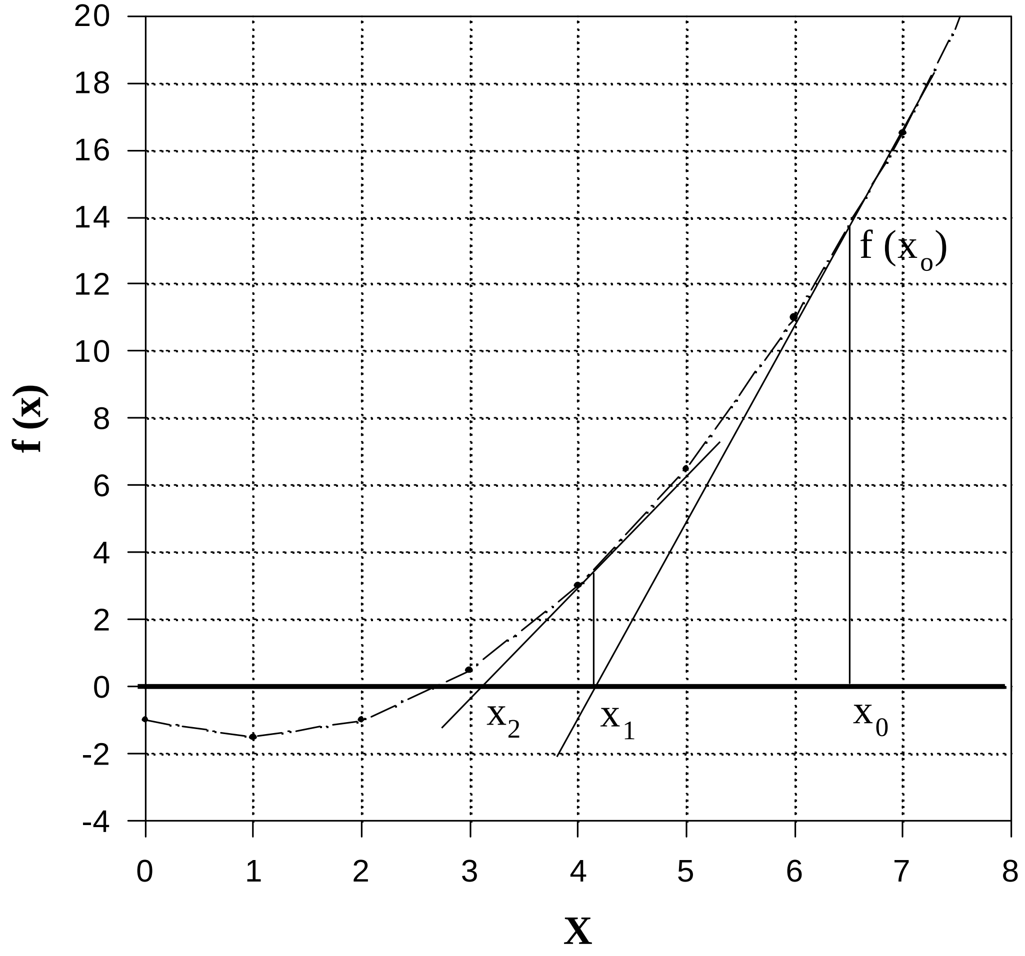
$$f\ (x)=a_o+a_1x+a_2x^2+\ldots+a_nx^n$$

must be solved by numerical methods. If the function is continuous on over the interval of interest one may solve for the condition f (x) = 0 by several methods. One is the bisection technique. In this method, two estimates of x are chosen so that $f(x_1)$™ 0 and f (x $_2$) – 0. By choosing subsequent values of x that are between the limits of x_1 and x_2, the root of x can be approached as closely as desired. This method will always work if the function is continuous on the interval, but may converge slowly. A more elegant method is the Newton-Raphson Technique. In this method an initial guess of the root x_0 is used. Then the slope of the line at the point f(x $_0$) is calculated and the point of intersection with the y axis is used as the next estimate of the root. This is illustrated in below.

In Newton's method the first guess (x_o) is the value of x used to evaluate $f(x_o)$ knowing the value of $f(x_o)$ the slope of the line tangent to the point $f(x_o),x_o$ is:

$$Slope=\frac{y_0-y_1}{x_0-x_1} \qquad \text{where: } \ y_1=0, \quad and \quad y_1=f\,(x_0)$$

Illustration of the Newton-Raphson method for solution of polynomials.



Review Questions

1. What is the electrical neutrality expression for the CO_2 -H_2O system ? For the calcite-gypsum system?

2. Define alkalinity? What is the expression for alkalinity in a calcite-water system? What assumptions if any have you made?

3. What are the pH limits in the calcite water system in relation to carbon dioxide pressure?

4. What is the Turner Effect?

5. Fly ash contains oxides of Ca, Na and K, which dissolve in water to form hydroxides. The least soluble of these is $Ca(OH)_2$. This hydroxide has a pH of approximately 12.5. However, the pH of calcium hydroxide after a time decreases. Why? What will the equilibrium pH be?

6. What are the two system points in the Johnston Diagram in your syllabus?

7. In the CO_2 - H_2O System the program to calculate pH etc. as a function of P_{CO2} contains the following code:

```
330  H2 = H1 - F/F1
```

What is this line doing. What is F and F1 ?

8. What will the addition of gypsum do to the pH of a calcite system in equilibrium with CO_2?

9. How does temperature and ionic strength affect CO_2-water, and CO_2-CaO-water systems?

10. When does Ca^{2+} act as an acid in soil systems ?

11. The calcium carbonate ion pairs are constant over some ranges of P_{co2} in the Johnston diagram but not others. Why?