Chemical Equilibria (continued)

Solubility Product

Like chemicals in reactions, solids and gasses also exist in equilibrium with water phases

$$A_aB_{b(solid)} \rightleftharpoons aA + bB \qquad \text{(ionization)}$$

At equilibrium, $\dfrac{[A]^a[B]^b}{\underbrace{[A_aB_b]_s}_{\text{usually incorporated directly into } K_{sp}}} = K_{sp}$

Typically $[A]^a[B]^b = K_{sp}$

K_{sp} is called the solubility product (it is unique for each species)

Gasses are explained using Henry's Law

$$A_{(g)} = K_H P_g$$

P_g — partial pressure of the gas

K_H is called the Henry's law constant. (it is unique for each gas-liquid system)

K_H varies with temperature and concentration of other materials (common-ion effect). Henry's law gives saturation values — Actual systems can be super- or sub- saturated

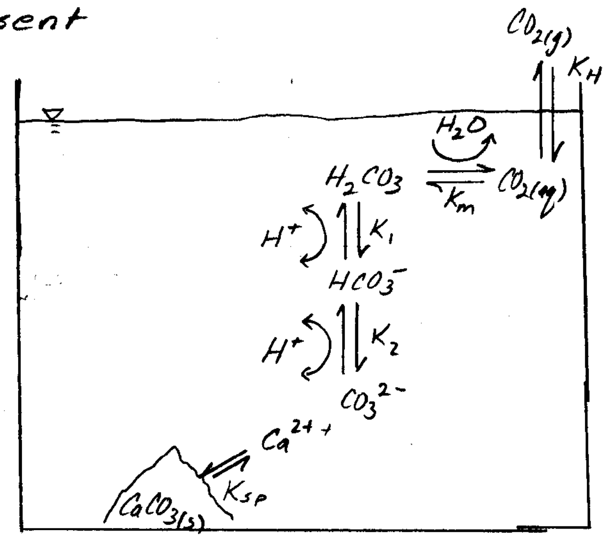
Carbonate System

The carbonate system is an important example of a gas-liquid, acid-base, liquid-solid equilibrium. It is important in environmental engineering because

- Buffers lakes and streams against pH changes from acidic inputs
- Influences CO_2 accumulation in the atmosphere and may effect global climate
- Plays role in Carbon cycling since photosynthesis (algae) and

other organisms obtain carbon for cell mass from carbonate species

Open carbonate system – solid present



Species present

- $CO_{2(g)}$
- $CO_{2(aq)}$ dissolved CO_2
- H_2CO_3 carbonic acid
- HCO_3^- bicarbonate
- CO_3^{2-} carbonate
- Ca^{2+} calcium ion
- $CaCO_3$ limestone

To determine equilibrium behavior of the system all equilibria & charge neutrality equations are constructed & solved simultaneously.

Henry's law relates $CO_{2(g)}$ & $CO_{2(aq)}$

① $[CO_{2(aq)}] = K_H P_{CO_2}$ $\qquad P_{CO_2} \approx 360 \cdot 10^{-6}$ atm

$K_H(@25°C) = 0.033363$

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

(1A) $\dfrac{[H_2CO_3]}{[CO_{2(aq)}]} = K_m = 1.58 \cdot 10^{-3}$

It is very difficult to differentiate $CO_{2(aq)}$ & H_2CO_3 so they are lumped together as $H_2CO_3^*$

$[H_2CO_3^*] = [H_2CO_3] + [CO_{2(aq)}] = [CO_{2(aq)}]\underbrace{(K_m + 1)}_{= 1.00158}$

$\therefore [H_2CO_3^*] = 1.00158\ K_H P_{CO_2}$

So the gas-liquid equilibrium is conviently expressed as

$$①^* \; [H_2CO_3^*] = 1.00158 \; K_H \; P_{CO_2} \qquad (@ 25°C) = (1.00158)(0.033363)(360 \cdot 10^{-6}) M$$

Now acid-base equilibria

② $H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$ $\qquad K_1 = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = 4.47 \times 10^{-7} M$

③ $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ $\qquad K_2 = \dfrac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.68 \times 10^{-11} M$

④ $H_2O \rightleftharpoons H^+ + OH^-$ $\qquad K_w = [H^+][OH^-] = 1 \cdot 10^{-14} M$

Now solid-liquid equilibria

⑤ $CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$ $\qquad K_{sp} = [Ca^{2+}][CO_3^{2-}] = 4.57 \cdot 10^{-9} M$

Finally charge balance

each mole of CO_3^{2-} can absorb 2 mole H^+

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

each mole Ca^{2+} can absorb 2 mole of e^-

Typically one is interested in speciation as a function of pH ($[H^+]$). Also the total carbonate concentration is usually of interest $\qquad C_{TOTAL} = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$

Depending on the tools available there are several ways to proceede with equilibrium calculations

Will illustrate how to proceede using a calculator

Rewrite equilibria in terms of common reference ion $[H^+]$

@25°C $[H_2CO_3^*] = 1.20297 \cdot 10^{-5} M$ (a constant in terms of $[H^+]$)

Equilibria

$$[HCO_3^-] = \frac{(4.47 \cdot 10^{-7})(1.20297 \cdot 10^{-5})}{[H^+]} = \frac{5.37726 \cdot 10^{-12}}{[H^+]}$$

$$[CO_3^{2-}] = \frac{(4.68 \cdot 10^{-11})(5.37726 \cdot 10^{-12})}{[H^+]^2} = \frac{2.51656 \cdot 10^{-22}}{[H^+]^2}$$

$$[Ca^{2+}] = \frac{(4.57 \cdot 10^{-9})}{[CO_3^{2-}]} = 1.81597 \cdot 10^{13} [H^+]^2$$

$$[OH^-] = \frac{1 \cdot 10^{-14}}{[H^+]} = \frac{1 \cdot 10^{-14}}{[H^+]}$$

Charge Balance

$$[H^+] + 2[Ca^{2+}] = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-]$$

$$[H^+] + 3.63195 \cdot 10^{13} [H^+]^2 = \frac{1 \cdot 10^{-14}}{[H^+]} + \frac{5.03311 \cdot 10^{-22}}{[H^+]^2} + \frac{5.37726 \cdot 10^{-12}}{[H^+]}$$

If one makes a substitution;

let $x = [H^+]$ and rearrange the charge balance

$$x + 3.63195 \cdot 10^{13} x^2 - 1 \cdot 10^{-14} x^{-1} - 5.03311 \cdot 10^{-22} x^{-2} - 5.37726 \cdot 10^{-12} x^{-1} = 0$$

the equation is in the form $f(x) = 0$ and can be solved using Newton's method:

$$x_{k+1} = x_k - \frac{f(x_k)}{\frac{df}{dx}(x_k)}$$

In this case we multiply $f(x)$ by x^2 to obtain:

$$f(x) = x^3 + 3.63195 \cdot 10^{13} x^4 - 1 \cdot 10^{-14} x - 5.03311 \cdot 10^{-22} - 5.37726 \cdot 10^{-12} x = 0$$

$$df/dx = 3x^2 + 4(3.63195 \cdot 10^{13}) x^3 - 1 \cdot 10^{-14} - 5.37726 \cdot 10^{-12}$$

An attached spreadsheet implements the solution (can also be done on a calculator)

	A	B	C	D	E	F
1	Newton's Method to find pH in Carbonate System					
2						
3	pH	x(k)=[H+]	f(x)	df/dx	Δx	x(k+1)=x(k)-f(x)/(df/dx))
4	5	1.00E-05	3.36E-07	1.34E-01	2.50E-06	7.50E-06
5	5.124938737	7.50E-06	1.06E-07	5.67E-02	1.88E-06	5.62E-06
6	5.249877473	5.62E-06	3.37E-08	2.39E-02	1.41E-06	4.22E-06
7	5.37481621	4.22E-06	1.06E-08	1.01E-02	1.05E-06	3.16E-06
8	5.499754947	3.16E-06	3.37E-09	4.26E-03	7.91E-07	2.37E-06
9	5.624693683	2.37E-06	1.07E-09	1.80E-03	5.93E-07	1.78E-06
10	5.749632419	1.78E-06	3.37E-10	7.58E-04	4.45E-07	1.33E-06
11	5.874571153	1.33E-06	1.07E-10	3.20E-04	3.34E-07	1.00E-06
12	5.999509883	1.00E-06	3.38E-11	1.35E-04	2.50E-07	7.51E-07
13	6.124448603	7.51E-07	1.07E-11	5.69E-05	1.88E-07	5.63E-07
14	6.2493873	5.63E-07	3.38E-12	2.40E-05	1.41E-07	4.22E-07
15	6.374325941	4.22E-07	1.07E-12	1.01E-05	1.06E-07	3.17E-07
16	6.49926445	3.17E-07	3.38E-13	4.27E-06	7.92E-08	2.38E-07
17	6.624202642	2.38E-07	1.07E-13	1.80E-06	5.94E-08	1.78E-07
18	6.749140085	1.78E-07	3.39E-14	7.61E-07	4.45E-08	1.34E-07
19	6.87407575	1.34E-07	1.07E-14	3.21E-07	3.34E-08	1.00E-07
20	6.999007198	1.00E-07	3.39E-15	1.35E-07	2.51E-08	7.52E-08
21	7.123928644	7.52E-08	1.07E-15	5.71E-08	1.88E-08	5.64E-08
22	7.248826372	5.64E-08	3.40E-16	2.41E-08	1.41E-08	4.23E-08
23	7.373667856	4.23E-08	1.07E-16	1.02E-08	1.06E-08	3.17E-08
24	7.498375999	3.17E-08	3.40E-17	4.30E-09	7.91E-09	2.38E-08
25	7.622768256	2.38E-08	1.07E-17	1.82E-09	5.91E-09	1.79E-08
26	7.746413709	1.79E-08	3.38E-18	7.70E-10	4.39E-09	1.35E-08
27	7.868302846	1.35E-08	1.06E-18	3.29E-10	3.22E-09	1.03E-08
28	7.986115112	1.03E-08	3.26E-19	1.43E-10	2.29E-09	8.04E-09
29	8.094761601	8.04E-09	9.66E-20	6.45E-11	1.50E-09	6.54E-09
30	8.1843412	6.54E-09	2.58E-20	3.23E-11	8.00E-10	5.74E-09
31	8.241011508	5.74E-09	5.09E-21	2.01E-11	2.54E-10	5.49E-09
32	8.260643781	5.49E-09	4.16E-22	1.68E-11	2.47E-11	5.46E-09
33	8.262602401	5.46E-09	3.69E-24	1.65E-11	2.23E-13	5.46E-09
34	8.262620155	5.46E-09	3.00E-28	1.65E-11	1.82E-17	5.46E-09
35	8.262620156	5.46E-09	0.00E+00	1.65E-11	0.00E+00	5.46E-09
36	8.262620156	5.46E-09	0.00E+00	1.65E-11	0.00E+00	5.46E-09

	A	B	C	D	E	F
1	Newton's Method					
2						
3	pH	x(k)=[H+]	f(x)	df/dx	Δx	x(k+1)=x(k)-f(x)/(df/dx))
4	=-LOG(B4)	=10^-5	=B4^3+33619500000000*B4^4-(0.00000000000001*B4)-(5.03311E-22)-(0.00000000000537726*B4)	=3*B4^2+4*33619500000000*B4^3-(0.00000000000001)-(0.00000000000537726)	=C4/D4	=B4-C4/D4
5	=-LOG(B5)	=F4	=B5^3+33619500000000*B5^4-(0.00000000000001*B5)-(5.03311E-22)-(0.00000000000537726*B5)	=3*B5^2+4*33619500000000*B5^3-(0.00000000000001)-(0.00000000000537726)	=C5/D5	=B5-C5/D5
6	=-LOG(B6)	=F5	=B6^3+33619500000000*B6^4-(0.00000000000001*B6)-(5.03311E-22)-(0.00000000000537726*B6)	=3*B6^2+4*33619500000000*B6^3-(0.00000000000001)-(0.00000000000537726)	=C6/D6	=B6-C6/D6
7	=-LOG(B7)	=F6	=B7^3+33619500000000*B7^4-(0.00000000000001*B7)-(5.03311E-22)-(0.00000000000537726*B7)	=3*B7^2+4*33619500000000*B7^3-(0.00000000000001)-(0.00000000000537726)	=C7/D7	=B7-C7/D7
8	=-LOG(B8)	=F7	=B8^3+33619500000000*B8^4-(0.00000000000001*B8)-(5.03311E-22)-(0.00000000000537726*B8)	=3*B8^2+4*33619500000000*B8^3-(0.00000000000001)-(0.00000000000537726)	=C8/D8	=B8-C8/D8
9	=-LOG(B9)	=F8	=B9^3+33619500000000*B9^4-(0.00000000000001*B9)-(5.03311E-22)-(0.00000000000537726*B9)	=3*B9^2+4*33619500000000*B9^3-(0.00000000000001)-(0.00000000000537726)	=C9/D9	=B9-C9/D9
10	=-LOG(B10)	=F9	=B10^3+33619500000000*B10^4-(0.00000000000001*B10)-(5.03311E-22)-(0.00000000000537726*B10)	=3*B10^2+4*33619500000000*B10^3-(0.00000000000001)-(0.00000000000537726)	=C10/D10	=B10-C10/D10
11	=-LOG(B11)	=F10	=B11^3+33619500000000*B11^4-(0.00000000000001*B11)-(5.03311E-22)-(0.00000000000537726*B11)	=3*B11^2+4*33619500000000*B11^3-(0.00000000000001)-(0.00000000000537726)	=C11/D11	=B11-C11/D11
12	=-LOG(B12)	=F11	=B12^3+33619500000000*B12^4-(0.00000000000001*B12)-(5.03311E-22)-(0.00000000000537726*B12)	=3*B12^2+4*33619500000000*B12^3-(0.00000000000001)-(0.00000000000537726)	=C12/D12	=B12-C12/D12
13	=-LOG(B13)	=F12	=B13^3+33619500000000*B13^4-(0.00000000000001*B13)-(5.03311E-22)-(0.00000000000537726*B13)	=3*B13^2+4*33619500000000*B13^3-(0.00000000000001)-(0.00000000000537726)	=C13/D13	=B13-C13/D13
14	=-LOG(B14)	=F13	=B14^3+33619500000000*B14^4-(0.00000000000001*B14)-(5.03311E-22)-(0.00000000000537726*B14)	=3*B14^2+4*33619500000000*B14^3-(0.00000000000001)-(0.00000000000537726)	=C14/D14	=B14-C14/D14
15	=-LOG(B15)	=F14	=B15^3+33619500000000*B15^4-(0.00000000000001*B15)-(5.03311E-22)-(0.00000000000537726*B15)	=3*B15^2+4*33619500000000*B15^3-(0.00000000000001)-(0.00000000000537726)	=C15/D15	=B15-C15/D15
16	=-LOG(B16)	=F15	=B16^3+33619500000000*B16^4-(0.00000000000001*B16)-(5.03311E-22)-(0.00000000000537726*B16)	=3*B16^2+4*33619500000000*B16^3-(0.00000000000001)-(0.00000000000537726)	=C16/D16	=B16-C16/D16
17	=-LOG(B17)	=F16	=B17^3+33619500000000*B17^4-(0.00000000000001*B17)-(5.03311E-22)-(0.00000000000537726*B17)	=3*B17^2+4*33619500000000*B17^3-(0.00000000000001)-(0.00000000000537726)	=C17/D17	=B17-C17/D17
18	=-LOG(B18)	=F17	=B18^3+33619500000000*B18^4-(0.00000000000001*B18)-(5.03311E-22)-(0.00000000000537726*B18)	=3*B18^2+4*33619500000000*B18^3-(0.00000000000001)-(0.00000000000537726)	=C18/D18	=B18-C18/D18
19	=-LOG(B19)	=F18	=B19^3+33619500000000*B19^4-(0.00000000000001*B19)-(5.03311E-22)-(0.00000000000537726*B19)	=3*B19^2+4*33619500000000*B19^3-(0.00000000000001)-(0.00000000000537726)	=C19/D19	=B19-C19/D19
20	=-LOG(B20)	=F19	=B20^3+33619500000000*B20^4-(0.00000000000001*B20)-(5.03311E-22)-(0.00000000000537726*B20)	=3*B20^2+4*33619500000000*B20^3-(0.00000000000001)-(0.00000000000537726)	=C20/D20	=B20-C20/D20
21	=-LOG(B21)	=F20	=B21^3+33619500000000*B21^4-(0.00000000000001*B21)-(5.03311E-22)-(0.00000000000537726*B21)	=3*B21^2+4*33619500000000*B21^3-(0.00000000000001)-(0.00000000000537726)	=C21/D21	=B21-C21/D21
22	=-LOG(B22)	=F21	=B22^3+33619500000000*B22^4-(0.00000000000001*B22)-(5.03311E-22)-(0.00000000000537726*B22)	=3*B22^2+4*33619500000000*B22^3-(0.00000000000001)-(0.00000000000537726)	=C22/D22	=B22-C22/D22
23	=-LOG(B23)	=F22	=B23^3+33619500000000*B23^4-(0.00000000000001*B23)-(5.03311E-22)-(0.00000000000537726*B23)	=3*B23^2+4*33619500000000*B23^3-(0.00000000000001)-(0.00000000000537726)	=C23/D23	=B23-C23/D23
24	=-LOG(B24)	=F23	=B24^3+33619500000000*B24^4-(0.00000000000001*B24)-(5.03311E-22)-(0.00000000000537726*B24)	=3*B24^2+4*33619500000000*B24^3-(0.00000000000001)-(0.00000000000537726)	=C24/D24	=B24-C24/D24
25	=-LOG(B25)	=F24	=B25^3+33619500000000*B25^4-(0.00000000000001*B25)-(5.03311E-22)-(0.00000000000537726*B25)	=3*B25^2+4*33619500000000*B25^3-(0.00000000000001)-(0.00000000000537726)	=C25/D25	=B25-C25/D25
26	=-LOG(B26)	=F25	=B26^3+33619500000000*B26^4-(0.00000000000001*B26)-(5.03311E-22)-(0.00000000000537726*B26)	=3*B26^2+4*33619500000000*B26^3-(0.00000000000001)-(0.00000000000537726)	=C26/D26	=B26-C26/D26
27	=-LOG(B27)	=F26	=B27^3+33619500000000*B27^4-(0.00000000000001*B27)-(5.03311E-22)-(0.00000000000537726*B27)	=3*B27^2+4*33619500000000*B27^3-(0.00000000000001)-(0.00000000000537726)	=C27/D27	=B27-C27/D27
28	=-LOG(B28)	=F27	=B28^3+33619500000000*B28^4-(0.00000000000001*B28)-(5.03311E-22)-(0.00000000000537726*B28)	=3*B28^2+4*33619500000000*B28^3-(0.00000000000001)-(0.00000000000537726)	=C28/D28	=B28-C28/D28
29	=-LOG(B29)	=F28	=B29^3+33619500000000*B29^4-(0.00000000000001*B29)-(5.03311E-22)-(0.00000000000537726*B29)	=3*B29^2+4*33619500000000*B29^3-(0.00000000000001)-(0.00000000000537726)	=C29/D29	=B29-C29/D29
30	=-LOG(B30)	=F29	=B30^3+33619500000000*B30^4-(0.00000000000001*B30)-(5.03311E-22)-(0.00000000000537726*B30)	=3*B30^2+4*33619500000000*B30^3-(0.00000000000001)-(0.00000000000537726)	=C30/D30	=B30-C30/D30
31	=-LOG(B31)	=F30	=B31^3+33619500000000*B31^4-(0.00000000000001*B31)-(5.03311E-22)-(0.00000000000537726*B31)	=3*B31^2+4*33619500000000*B31^3-(0.00000000000001)-(0.00000000000537726)	=C31/D31	=B31-C31/D31
32	=-LOG(B32)	=F31	=B32^3+33619500000000*B32^4-(0.00000000000001*B32)-(5.03311E-22)-(0.00000000000537726*B32)	=3*B32^2+4*33619500000000*B32^3-(0.00000000000001)-(0.00000000000537726)	=C32/D32	=B32-C32/D32
33	=-LOG(B33)	=F32	=B33^3+33619500000000*B33^4-(0.00000000000001*B33)-(5.03311E-22)-(0.00000000000537726*B33)	=3*B33^2+4*33619500000000*B33^3-(0.00000000000001)-(0.00000000000537726)	=C33/D33	=B33-C33/D33
34	=-LOG(B34)	=F33	=B34^3+33619500000000*B34^4-(0.00000000000001*B34)-(5.03311E-22)-(0.00000000000537726*B34)	=3*B34^2+4*33619500000000*B34^3-(0.00000000000001)-(0.00000000000537726)	=C34/D34	=B34-C34/D34
35	=-LOG(B35)	=F34	=B35^3+33619500000000*B35^4-(0.00000000000001*B35)-(5.03311E-22)-(0.00000000000537726*B35)	=3*B35^2+4*33619500000000*B35^3-(0.00000000000001)-(0.00000000000537726)	=C35/D35	=B35-C35/D35
36	=-LOG(B36)	=F35	=B36^3+33619500000000*B36^4-(0.00000000000001*B36)-(5.03311E-22)-(0.00000000000537726*B36)	=3*B36^2+4*33619500000000*B36^3-(0.00000000000001)-(0.00000000000537726)	=C36/D36	=B36-C36/D36

An alternate approach is to simply create a spreadsheet that computes each equilibrium speciation as a function of pH, then choose the pH that satisfies the charge balance.

This method is illustrated on the attached spreadsheet.

Other carbonate "systems"

<u>pH of rainwater (open system – no solid present)</u>.

$[H_2CO_3^*] = 1.00158\, K_H P_{CO_2}$ ← Carbon source

$$\left.\begin{aligned}[HCO_3^-] &= K_1 [H_2CO_3^*][H^+]^{-1} \\ [CO_3^{2-}] &= K_2 [HCO_3^-][H^+]^{-1} \\ [OH^+] &= K_w [H^+]^{-1}\end{aligned}\right\} \text{equilibria}$$

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \quad \} \text{ charge}$$

Result after similar calculations is $pH \approx 5.6$

<u>pH in aquifer (closed system – solid present)</u>
Initially water enters aquifer (limestone $CaCO_{3(s)}$) as rainwater in equilibrium with atmosphere.

In this case a mass balance is required to develop the equilibrium system. Because nearly all

water	$H_2CO_3^*$ H^+ HCO_3^- OH^- Ca^{2+} CO_3^{2-}
solid	$CaCO_{3(s)}$

carbonate must come from dissolution of aquifer ($H_2CO_3^*$ entering in rainwater is negligible), each Ca^{2+} in solution is matched with a CO_3^{2-} in solution. Once in solution the CO_3^{2-} engages in various acid-base equilibria, but the <u>Total Carbonate</u> in solution must equal the Total Calcium in solution

	A	B	C	D	E	F	G	H	I	J
1	1.20297E-05									
2	5.37726E-12									
3	2.51656E-22									
4	1.81597E+13									
5										
6	3.63195E+13									
7	5.03311E-22									
8			Carbonate System with Solid Present							
9	[H+]	pH	[HCO3*]	[HCO3]	[CO3]	[Ca}	[OH]	Charge+	Charge-	Δcharge
10	1.00E+00	0	1.20297E-05	5.38E-12	2.52E-22	1.82E+13	1.00E-14	3.63E+13	5.39E-12	3.63E+13
11	1.00E-02	2	1.20297E-05	5.38E-10	2.52E-18	1.82E+09	1.00E-12	3.63E+09	5.39E-10	3.63E+09
12	1.00E-03	3	1.20297E-05	5.38E-09	2.52E-16	1.82E+07	1.00E-11	3.63E+07	5.39E-09	3.63E+07
13	1.00E-04	4	1.20297E-05	5.38E-08	2.52E-14	1.82E+05	1.00E-10	3.63E+05	5.39E-08	3.63E+05
14	1.00E-05	5	1.20297E-05	5.38E-07	2.52E-12	1.82E+03	1.00E-09	3.63E+03	5.39E-07	3.63E+03
15	1.00E-06	6	1.20297E-05	5.38E-06	2.52E-10	1.82E+01	1.00E-08	3.63E+01	5.39E-06	3.63E+01
16	1.00E-07	7	1.20297E-05	5.38E-05	2.52E-08	1.82E-01	1.00E-07	3.63E-01	5.39E-05	3.63E-01
17	1.00E-08	8	1.20297E-05	5.38E-04	2.52E-06	1.82E-03	1.00E-06	3.63E-03	5.44E-04	3.09E-03
18	8.00E-09	8.09691	1.20297E-05	6.72E-04	3.93E-06	1.16E-03	1.25E-06	2.32E-03	6.81E-04	1.64E-03
19	6.00E-09	8.2218487	1.20297E-05	8.96E-04	6.99E-06	6.54E-04	1.67E-06	1.31E-03	9.12E-04	3.96E-04
20	5.00E-09	8.30103	1.20297E-05	1.08E-03	1.01E-05	4.54E-04	2.00E-06	9.08E-04	1.10E-03	-1.90E-04
21	5.50E-09	8.2596373	1.20297E-05	9.78E-04	8.32E-06	5.49E-04	1.82E-06	1.10E-03	9.96E-04	1.03E-04
22	5.41E-09	8.2668027	1.20297E-05	9.94E-04	8.60E-06	5.32E-04	1.85E-06	1.06E-03	1.01E-03	5.00E-05
23	4.00E-09	8.39794	1.20297E-05	1.34E-03	1.57E-05	2.91E-04	2.50E-06	5.81E-04	1.38E-03	-7.97E-04
24	1.00E-10	10	1.20297E-05	5.38E-02	2.52E-02	1.82E-07	1.00E-04	3.63E-07	1.04E-01	-1.04E-01

Thus in the aquifer we have

$$\left.\begin{aligned} [H_2CO_3^*] &= \frac{[H^+][HCO_3^-]}{K_1} \\ [HCO_3^-] &= \frac{[H^+][CO_3^{2-}]}{K_2} \end{aligned}\right\} \text{carbonate equilibria}$$

$$[CO_3^{2-}] = \frac{K_{sp}}{[Ca^{2+}]} \quad \} \text{ limestone dissolution}$$

$$[OH^-] = K_w [H^+]^{-1} \quad \} \text{ water dissociation}$$

$$[H^+] + 2[Ca^{2+}] = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] \quad \} \text{ charge balance}$$

$$[Ca^{2+}] = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \quad \} \text{ material balance}$$

Using similar analyses as before one can write an equation in terms of $[H^+]$ and determine the resulting equilibrium pH.

In this case the result is $pH \approx 9.9$