CIVE 3331 Environmental Engineering

CIVE 3331 - ENVIRONMENTAL ENGINEERING
Spring 2003

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Environmental Chemistry

Most environmental engineering problems require some comfort and familiarity with chemistry.

With the exception of noise and thermal pollution, all pollution problems have a chemical basis (and

sometimes a chemical solution). This part of the course is a brief re-familarization with important

chemistry concepts that you have already had in depth in your one year of college chemistry (typically

taken as a freshman or sophomore).

Stochiometry

Stochiometry is the measurement of how chemicals combine with each other in reactions. It is the

reaction equivalent of a mass balance. Usual units are moles of combining chemicals, but masses can

also be used and the results are the same (when adjusted for molecular weights). Chemicals in reactions

are classified into two categories: reactants and products.   Assuming a reaction is essentially

irreversible, the reactants are usually written on the left side of a chemical "equation" and the products

CIVE 3331 Environmental Engineering

on the right side. If the reaction is reversible, the designation reactant and product is more nebulus, depending on the preferred direction of the reaction under the particular conditions. The conservation of mass requires that the the masses of products equal the masses of reactants for a chemical equation to be "balanced."

Consider the oxidation of methane (sewer gas). $CH_4 + O_2 \Rightarrow CO_2 + H_2O$ (+ heat). The left side is not balanced with the right side because there are 4 H on the left and only 2 H on the right, and 2 O on the laft and 3 O on the right. A balanced equation has equal numbers of atomic species on each side. One approach for simple reactions involving organic compounds (materials containing Carbon) is

1. Balance carbon with carbon

2. Balance H with water.

3. Balance O with O.

Returning to our example:

$CH_4 + O_2 \Rightarrow CO_2 + H_2O$ (+ heat)

1. Carbons are balanced.

2. 4 H on left, balance with total of 2 H_2O on right.

$CH_4 + O_2 \Rightarrow CO_2 + 2H_2O$ (+ heat)
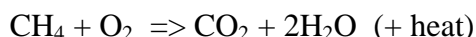
3. Balance 4 O on right with 2 O_2 on left.

$CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O$ (+ heat)
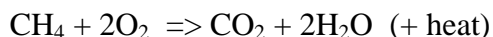
Now if we were interested in masses instead of moles reacting we can use these stochiometric relationships and the atomic masses of each species to determine the masses involved.

C=12, O=16, H=1 grams/mole
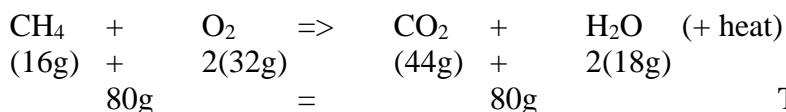
CH_4	+	O_2	=>	CO_2	+	H_2O	(+ heat)
(16g)	+	2(32g)		(44g)	+	2(18g)	
	80g		=		80g		Thus the masses balance!

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Many environmental problems involve substances dissolved in water. One concentration unit used is moles/liter. (M or mole/L) This unit can be used directly in stochiometric relationships, other concentration units must be converted using the atomic wieghts of the compounds.

One measure of water pollution is the oxygen demand – it is one measure of the ability of a body of water to assimilate (use up) waste materials. One kind of oxygen demand (there are several) is the theoretical oxygen demand (ThOD) – the amount of oxygen required to exactly (stochiometrically) oxidize a compound.

As an example of using a concentration unit in stochiometric equations consider the theoretical oxidation of a solution of 1.67 mM (millimolar) solution of glucose ($C_6H_{12}O_6$). Complete oxidation of a carbohydrate (C,H, and O – think of carbon and water its in the name!) produces CO_2 and H_2O and nothing else. Find the amount of oxygen required to completely oxidize this solution (ThOD).

1. Write the reaction:

$$C_6H_{12}O_6 \quad + \quad O_2 \quad = \quad CO_2 \quad + \quad H_2O$$

2. Balance the reactants and products

   a. Balance carbons (6 CO_2 on right to balance 6 C on left)

   $$C_6H_{12}O_6 \quad + \quad O_2 \quad = \quad 6CO_2 \quad + \quad H_2O$$

   b. Balance hydrogen (6 H_2O on right to balance 12 H on left)

   $$C_6H_{12}O_6 \quad + \quad O_2 \quad = \quad 6CO_2 \quad + \quad 6H_2O$$
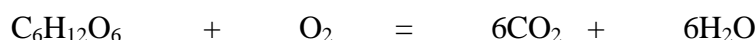
   c. Balance oxygen (6 O_2 on left plus the 6O in the sugar to balance the total of 18 O on right

   $$C_6H_{12}O_6 \quad + \quad 6O_2 \quad = \quad 6CO_2 \quad + \quad 6H_2O$$
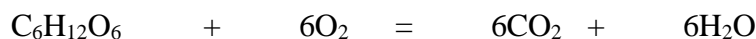
3. Now express in appropriate units.

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a. It takes 6 moles of O_2 to oxidize one mole of glucose. So we need 6 (1.67 mM) of O_2 to

oxidize the solution or 10.02mM-O_2 (could also write mmol/L).

b. To convert to mass basis use the atomic weight of O_2 = 32g/mole:

$$\frac{10.02 mmol - O_2}{L} \times \frac{0.032g}{1mmol - O_2} = \frac{0.32g - O_2}{L} = 320mg / L - O_2$$

Enthalpy in Chemical Systems

The balance of energy in chemical reactions is usually explained and quantified using the

principle of enthalpy.   Most chamical reactions of interests to civil engineers are constant pressure

reactions, so that the energy balance is :

$U_1 + Q_{heat} = U_2 + W_{work}$

$\Delta U = \Delta H - p\Delta V$

The last term is the work done by the system. Substitute the second equation into the energy equation

(the first equation)

$U_1 + Q_{heat} = U_2 + W_{work} = U_2 + \Delta H - \Delta U$

Rearrange as

$Q_{heat} = U_2 - U_1 + \Delta H - \Delta U$; but $U_2 - U_1 = \Delta U$ so $Q_{heat} = \Delta H$

Thus in a chemical reaction the heat liberated or absorbed is usually equal to the change in enthalpy of

the chemical system.
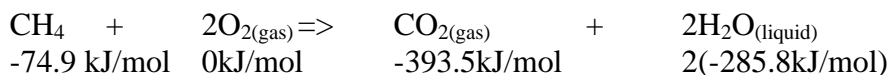
1. If $\Delta H > 0$ heat is absorbed (added) and the reaction is called endothermic (needs heat).

2. If $\Delta H < 0$ heat is liberated (released) and the reaction is called exothermic (gives heat).

The change in enthalpy is called the heat of the reaction. The change is more important than the

absolute enthalpy, so most discussions are referenced against a set of standard enthalpies.

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Notation is H_{298}^{o} = enthalpy of H at 1 atm, 298K.

A table of standard enthalpies can be used to determine if a reaction requires heat or liberates heat.

$$CH_4 \quad + \quad 2O_{2(gas)} => \quad CO_{2(gas)} \quad + \quad 2H_2O_{(liquid)}$$

-74.9 kJ/mol   0kJ/mol   -393.5kJ/mol   2(-285.8kJ/mol)

Net (Products - Reactants) = -890.2kJ/mol CH_4. Since $\Delta H < 0$ the reaction liberates heat.

Enthalpy is also used to explain energetics in photochemical reactions. Such reactions are fundamental in understanding air pollution. In a photochemical reaction the added energy (heat) is light. One kind of photochemical reaction is photolysis (photo – light; lysis – split) where the light energy splits a compound into other compounds. The heat energy in light is related to the wavelength (color) of the light.

E(Joules/photon) = $h\nu = hc/\lambda$; h is Plank's constant. One typical calculation is to determine the wavelength of light required to cause photolysis of a chemical, for example ozone. We use the required change in enthalpy to determine how much energy is needed, then use the energy-wavelength equation to determine the longest wavelength light that can produce the required energy. One needs 6.02 x 10^{23} photons to energize one mole of reactant.

E (J/mole)= 6.02 x 10^{23}(photons/mole) *(J/photon)= 6.02 x 10^{23} *hc/λ (J/mole)

Observe as the wavelength gets bigger, the energy per mole of photons decreases, so in dealing with light energized reactions we will usually be using inequalities.

Now to examine Ozone.

O$_3$ +   heat   =>   O$_2$ +   O

142.9kJ/mol   (0)   247.5kJ/mol
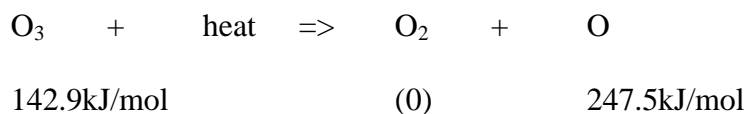
ΔH = 247.5-142.9=104.6 kJ/mol > 0 so reaction requires heat.   Now using the light relationship we have:

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$6.02 \times 10^{23} * hc/l$ (J/mol) $> 104.6 * 10^3$ J/mol

This inequality says that the mole of photons mush have at least enough energy to stimulate the reaction, and we can now solve for the biggest wavelength that will have enough energy.

$6.02 \times 10^{23} * hc/l > 104.6 * 10^3$

$(6.02 \times 10^{23} * hc) / (104.6 * 10^3) > l$

$((6.02 \times 10^{23} * 6.6 \times 10^{-34}$ J s/mole$)(3 \times 10^8$ m/s$)) / (104.6 * 10^3$ J/mole$) > l = 1.1 \times 10^{-6}$ m

Thus a wavelength of about 1 micrometer (micron) or smaller is sufficient to energize ozone into diatomic oxygen and mono-atomic oxygen. This reaction illustrates how high altitude ozone protects the surface of Earth from high energy, short wavelength radiation (by absorbing the energy).

Chemical Equilibria

The reactions studied so far are written as if they proceed in one direction – most reactions are reversible to some extent. When the forward rates equal the reverse rates the reaction is in equilibrium – we observe no change in quantities on either side of the reaction.

A generic reaction might be:

$$aA \quad + \quad bB \quad \Leftrightarrow \quad cC \quad + dD$$

We could study the rate of change of any species as: $-\dfrac{dA}{dt}; -\dfrac{dB}{dt}; \dfrac{dC}{dt}; \dfrac{dD}{dt}$ all 4 expressons are "rates"

but the values of the rates are not necessarily the same. Stochiometry provides a normalization

procedure: $-\dfrac{a}{a}\dfrac{dA}{dt} = -\dfrac{a}{b}\dfrac{dB}{dt} = \dfrac{a}{c}\dfrac{dC}{dt} = \dfrac{a}{d}\dfrac{dD}{dt}$; in this case the reference species is A.

This normalization means that a moles of A disappears in one time unit as a/c units of C appear in the same time interval. One can use any of the species as the reference species, depending on the needs of the particular problem.

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At equilibrium the rates vanish ; $\frac{dA}{dt} = \frac{dB}{dt} = \frac{dC}{dt} = \frac{dD}{dt} = 0$ and the concept called the "law of mass action" is used to study the relationship between products and reactants.

The quotient $Q = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ is the ratio of products activities (concentrations in our course) to reactants activities. At equilibrium $Q = K$, K is called the equilibrium constant. For a given reaction knowledge of Q and K tells us the state of the system and the likely direction that the reaction will proceed.

1. $Q = K$; the reaction is in equilibrium.

2. $Q < K$; the reaction is not in equilibrium, reaction is likely to proceed forward as written.

3. $Q > K$; the reaction is not in equilibrium, reaction is likely to proceed backward as written

Typically the equilibrium expression is written as

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \ .$$

The terms in the square brackets are called activities, in dilute systems the activities and molar concentrations are roughly equivalent.   Depending on what kind of reaction is being studied the *name* given to the equilibrium constant varies.

1. If the reaction is dissolution/precipitation of a solid, K is called the solubility product.

2. If the reaction is disassociation of an ionic compound (HCl for instance), K is called the ionization constant.

3. If the reaction is the dissolution/volatilization of a gas into a liquid, K is usually Henry's Law constant.

The constants are often expressed as their negative base-10 logarithms and the notation convention using a lower case "p" is used (just like *pH* of hydrogen ion concentration): $pK = - log_{10} K$; $K = 10^{-pK}$

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Acid Base Reactions

Water dissociates slightly, so that there are some hydrogen ions (H^+) in solution as well as hydroxide

ions (OH^-). The "reaction" is written as $H_2O \Leftrightarrow H^+ + OH^-$. The law of mass action is:

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

The molar concentration of water in water (the denominator) is about 55 mol/L (or 55M). When one

part of the law of mass action is huge compared to the rest of the terms, it is usually absorbed into the

constant (and the constant is given a special name – in this case the disassociation constant for water).

$$K_w = K[H_2O] = [H_2O]\frac{[H^+][OH^-]}{[H_2O]} = [H^+][OH^-] = 1\times10^{-14}$$

Expressed in negative logarithm form the constant is

$$pK_w = -\log(K_w) = pH + pOH = 14$$

In a neutral solution, the hydrogen and hydroxide ion concentrations are the same so *pH = pOH*. Thus

if these two values are equal and sum to 14, then *pH = 7* or $[H^+]=10^{-7}M$.

An acidic solution is where $[H^+] > [OH^-]$; *pH < pOH*; *pH < 7*

A basic solution is where $[H^+] < [OH^-]$; *pH > pOH*; *pH > 7*

pH is a central, fundamental concept in environmental chemistry, and you must be able to convert

between *pH* and [H+] almost without a second thought. *pH* control is often a major process feature in

treating waste streams or protecting the receiving media for wastes.

pH Control

Ammonia stripping is an example that illustrates the importance of *pH* control and how to make the

associated computations. Ammonia gas is relatively insoluble in water (it will separate from the water

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and enter the atmosphere with very little provocation!). One way to remove ammonium ions from water (which are soluble) is to adjust the pH so that the gas concentration is large and the water becomes supersaturated with ammonia and the excess ammonia effervesces.

The "reaction" to consider is

$$NH_3 \quad + \quad H_2O \quad \Leftrightarrow \quad NH_4^+ \quad + \quad OH^-$$

The ammonium ion is the nitrogen compound on the right hand side of the equation; ammonia gas is on the left. The law of mass action for this expression is

$$K_{NH_3} = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.82 \times 10^{-5} M$$

If we can make the hydroxide ion concentration large and if equilibrium is maintained, then the ammonium ion will be small and the ammonia concentration will be relatively large – the situation we want for the gas to leave the water. That is we want to shift the reaction to the left os we want to try to make Q > K. With these ideas we can develop a design curve to express various equilibrium relationships as a function of *pH*.

First we incorporate the water disassociation term into the equilibrium expression (by convention we usually express these kind of cases in *pH* and not *pOH*).

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{[NH_4^+][1\times10^{-14}]}{[NH_3][1\times10^{-pH}]} = 1.82\times10^{-5} M$$

Now express the ratio of ammonium ion to ammonia as:

$$\frac{[NH_4^+]}{[NH_3]} = \frac{[1.82\times10^{-5}][1\times10^{-pH}]}{[1\times10^{-14}]}$$

Now express the ammonia fraction in terms of total nitrogen compounds in the water as:

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$$\frac{[NH_3]}{[NH_3]+[NH_4^+]} = \frac{1}{1+\dfrac{[NH_4^+]}{[NH_3]}} \times 100\% = \frac{1}{1+\dfrac{[1.82\times10^{-5}][1\times10^{-pH}]}{[1\times10^{-14}]}} \times 100\%$$

Now at this point it is useful to construct a spreadsheet (or program your calculator) to plot the %-ammonia as a function of *pH*.

	A	B	C	D	E	F	G	H	I	J
1	Ammonia Stripping Example									
2										
3	K_NH3	1.82E-05	M							
4	K_w	1.00E-14	M							
5										
6	pH	[H]	[NH4/NH3]	[NH3_%]						
7	1	0.1	1.82E+08	0.0%						
8	1.5	0.03162278	5.76E+07	0.0%						
9	2	0.01	1.82E+07	0.0%						
10	2.5	0.00316228	5.76E+06	0.0%						
11	3	0.001	1.82E+06	0.0%						
12	3.5	0.00031623	5.76E+05	0.0%						
13	4	0.0001	1.82E+05	0.0%						
14	4.5	3.1623E-05	5.76E+04	0.0%						
15	5	0.00001	1.82E+04	0.0%						
16	5.5	3.1623E-06	5.76E+03	0.0%						
17	6	0.000001	1.82E+03	0.1%						
18	6.5	3.1623E-07	5.76E+02	0.2%						
19	7	0.0000001	1.82E+02	0.5%						
20	7.5	3.1623E-08	5.76E+01	1.7%						
21	8	0.00000001	1.82E+01	5.2%						
22	8.5	3.1623E-09	5.76E+00	14.8%						
23	9	1E-09	1.82E+00	35.5%						
24	9.5	3.1623E-10	5.76E-01	63.5%						
25	10	1E-10	1.82E-01	84.6%						
26	10.5	3.1623E-11	5.76E-02	94.6%						
27	11	1E-11	1.82E-02	98.2%						
28	11.5	3.1623E-12	5.76E-03	99.4%						
29	12	1E-12	1.82E-03	99.8%						
30	12.5	3.1623E-13	5.76E-04	99.9%						
31	13	1E-13	1.82E-04	100.0%						
32	13.5	3.1623E-14	5.76E-05	100.0%						
33	14	1E-14	1.82E-05	100.0%						
34										

Figure #.# Ammonia Stripping Design

Figure 1. Ammonia Stripping Spreadsheet Example (AmmoniaStrip.XLS)

From the curve in Figure 1, we observe that at neutral pH, or acidic conditions that there is very little ammonia in solution, all the nitrogen is in the ammonium-ion form. As we increase pH (make the solution basic) the solution becomes enriched with ammonia – which is then easy to strip in a counter current air stripping tower or something similar. PH control is remarkably important in environmental engineering, although conceptually simple it is sometimes hard to do. When dealing with toxic metals,

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the pH can determine which "version" of the metals will dissolve, or if the metals will dissolve at all –

some versions are much less toxic than others.

Solubility Product

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

$$A_a B_{b(solid)} \Leftrightarrow aA + bB \quad (ioniation)$$
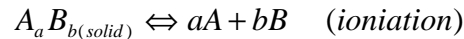
At equilibrium the law of mass action is:

$$K = \frac{[A]^a [B]^b}{[A_a B_b]}; K_{sp} = [A]^a [B]^b$$

The solid phase molar concentration is usually incorporated into the constant, which is K_{sp}, and is called

the solubility product. It is unique for each species.

Gasses are explained using Henry's law, which is a law of mass action expressed in partial

pressures.

$$[A] = K_{H\_A} P_A$$

The Henry's law constant is temperature dependent and the common-ion effect is significant in gas

dissolution – that is the presence of other gasses impacts the process. Henry's law gives saturation

values, actual systems can easily be super- or sub- saturated with respect to the particular gas and be

relatively stable for long times.

Carbonate System

The carbonate system is an important example os a gas-liquid, acid-base, liquid-solid

equilibrium system. It is extremely important in environmental engineering because:

1. Carbonate buffers lakes and streams against pH changes from acidic inputs (acid rain).

2. Influences CO2 accumulation in the atmosphere and may affect global climate.

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3. Plays a role in carbon cycling. Algae (photosynthesis) and other organisms obtain carbon for cell mass from some carbonate compounds.

Analysis example.

Open carbonate system, solid present. Goal will be to develop a mathematical expression that relates pH and concentration of various species in solution. The system is open to the atmosphere, and there is excess solid present in the aqueous phase.

Step 1: Sketch the system
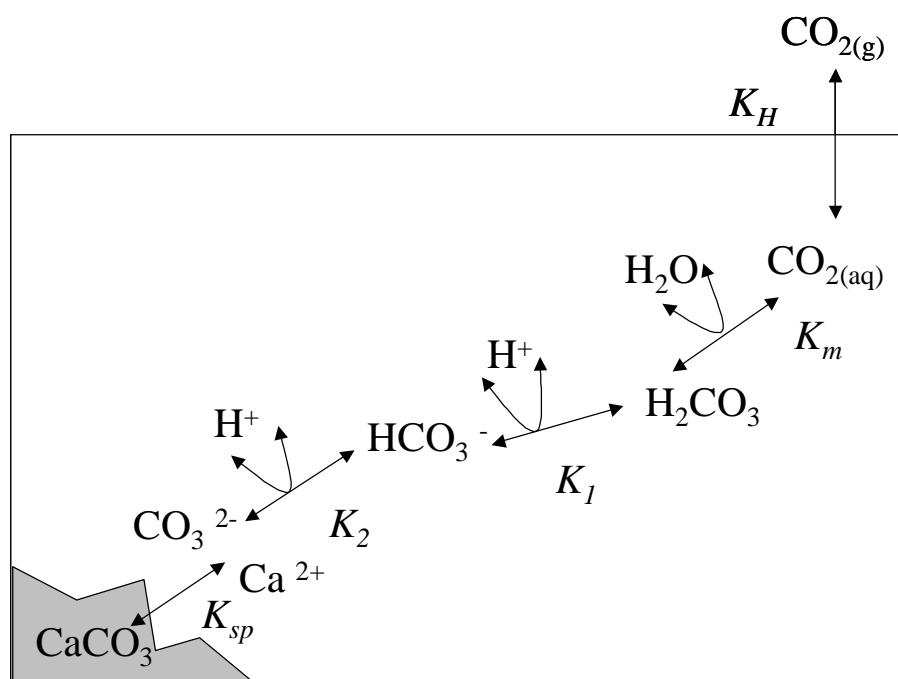
Figure 2. Open Carbonate System - Solid Present

Step 2: List the species that are present:

1. CO_2 (g) atmospheric

2. CO_2 (aq) dissolved

3. H_2CO_3 (carbonic acid)

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4. HCO_3^-

5. CO_3^{2-}

6. Ca^{2+}

7. $CaCO_3$

Step 3: To determine the equilibrium behavior of the system all equilibria and charge neutrality

equations are constructed, then solved simultaneously.

Henry's Law

$$[CO_{2(aq)}] = K_H P_{CO_2}$$
$$P_{CO_2} = 360 \times 10^{-6} atm$$
$$K_H = 0.033363 (@ 25^0 C)$$

CO2 dissolved-carbonic acid equilibrium

$$\frac{[H_2CO_3]}{[CO_{2(aq)}]} = K_m = 1.58 \times 10^{-3} M$$

It is very difficult to differentiate between dissolved CO_2 and carbonic acid analytically so these two

species are usually combined as $H_2CO_3^*$

$$[H_2CO_3^*] = [H_2CO_3] + [CO_{2(aq)}] = [CO_{2(aq)}](K_m + 1) = 1.00158M$$
$$[H_2CO_3^*] = 1.00158 K_H P_{CO_2}$$

So we now have the gas-liquid equilibrium in terms of partial pressure of gas over the water. If we

insert numerical values we will have

$$[H_2CO_3^*] = 1.00158(0.033363)(360 \times 10^{-6})M$$

Now for the three acid-base type equilibria

$$H_2CO_3^* \Leftrightarrow H^+ + HCO_3^- \quad K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = 4.47 \times 10^{-7} M$$

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$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \quad K_2 = \frac{[H^+][CO_3^{2-}]}{[H\ CO_3^-]} = 4.68 \times 10^{-11} M$$

$$H_2O \Leftrightarrow H^+ + OH^- \quad K_w = [H^+][OH^-] = 1 \times 10^{-14} M$$
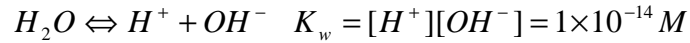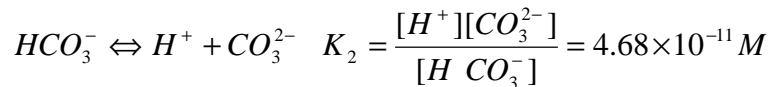
Now for the solid-liquid equilibrium

$$CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-} \quad K_{sp} = [Ca^{2+}][CO_3^{2-}] = 4.57 \times 10^{-9} M$$
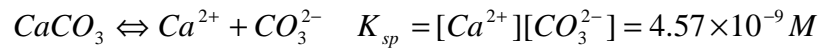
Finally the charge balance

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

In the charge balance, each mole of Ca supplies two moles of positive charges, each mole of carbonate

provides two moles of negative charge, while each mole of bicarbonate provides one mole of negative

charge.

Typically we are interested in speciation as a function of pH, and the total carbon concentrations are

also of interest.

$$C_{total} = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3^*]$$
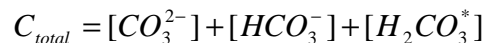
Depending on what tools are available there are several ways to proceed with equilibrium calculations.

If we are using a hand calculator we might express each equation in logarithmic fashion and solve the

resulting cubic equation(s). Alternatively we can proceed in the arithmetic space as:

Rewrite in terms of common reference species (H+). Then insert the results into the charge balance

equation, The charge balance in this case becomes a cubic equation in [H+] after we observe that [H+]

cannot be zero (and make sense).

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$$[H_2CO_3^*] = 1.20297 \times 10^{-5} M$$

$$[HCO_3^-] = \frac{(4.47E-07)(1.20297E-5)}{[H+]} = \frac{5.37726E-12}{[H+]}$$

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

$$[Ca^{2+}] = \frac{4.57E-09}{[CO_3^{2-}]} = 1.81597E-13 \times [H+]^2$$

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

$$[H^+] + 2[Ca^{2+}] = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] \Rightarrow [H^+] + 3.63195E-13[H+]^2$$

$$= \frac{1E-14}{[H+]} + 2 \times \frac{2.51656E-22}{[H+]^2} + \frac{5.37726E-12}{[H+]}$$

Now rearrangement of the charge balance with x = [H+] produces

$$x + 3.63195E+13x^2 - (1E-14)x^{-1} - (5.03311E-22)x^{-2} - (5.37726E-12)x^{-1} = 0$$

Now multiply through by x² (recall that x = 0 does not make sense, so no need to worry about this solution to the equation)

$$x^3 + 3.63195E+13x^4 - (1E-14)x - (5.03311E-22) - (5.37726E-12)x = 0$$

This equation has the form *f(x)=0* so we can solve by Newton's method.

We need the derivative of *f(x)*

$$f(x) = x^3 + 3.63195E+13x^4 - (1E-14)x - (5.03311E-22) - (5.37726E-12)x$$
$$\frac{df}{dx}(x) = 3x^2 + 4(3.63195E+13)x^3 - (1E-14) - (5.37726E-12)$$

Newton's method starts with a reasonable guess for x (any non-zero value should work) and applies the following update equation repeatedly until the guess stops changing (or the algorithm fails).

CIVE 3331 Environmental Engineering

$$x^{k+1} = x^k - \frac{f(x^k)}{\frac{df}{dx}(x^k)}$$

Figure 3 is a spreadsheet that implements Newton's method to find the value of pH that satisfies

$f(10^{-pH}) = 0$.

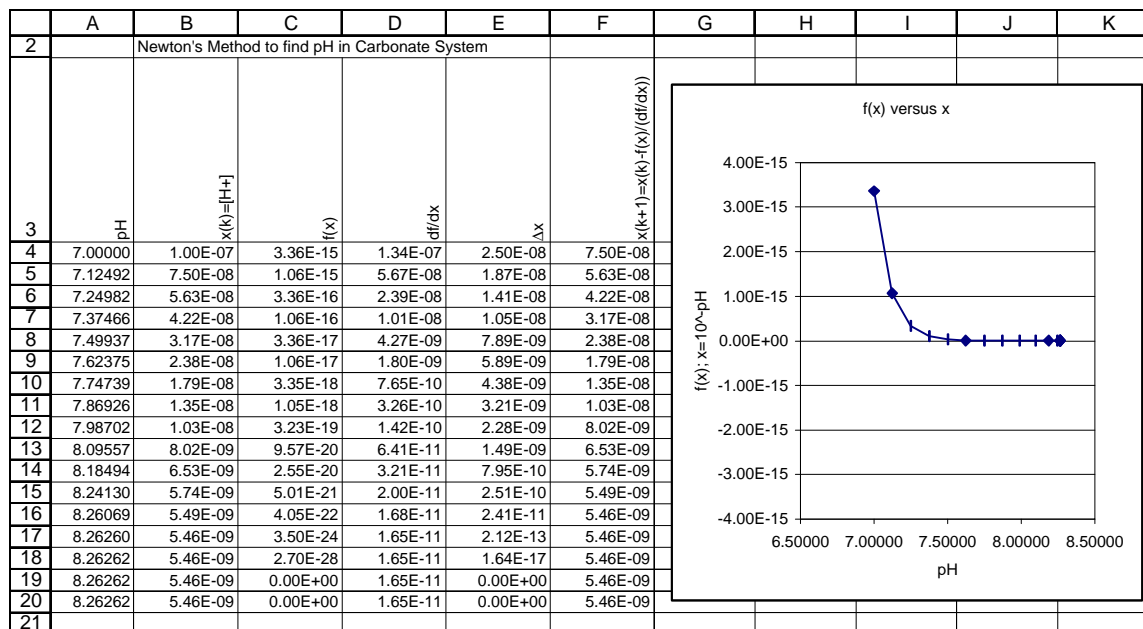|	A	B	C	D	E	F	G	H	I	J	K
2		Newton's Method to find pH in Carbonate System									
3	pH	x(k)=[H+]	f(x)	df/dx	Δx	x(k+1)=x(k)-f(x)/(df/dx))			f(x) versus x		
4	7.00000	1.00E-07	3.36E-15	1.34E-07	2.50E-08	7.50E-08					
5	7.12492	7.50E-08	1.06E-15	5.67E-08	1.87E-08	5.63E-08					
6	7.24982	5.63E-08	3.36E-16	2.39E-08	1.41E-08	4.22E-08					
7	7.37466	4.22E-08	1.06E-16	1.01E-08	1.05E-08	3.17E-08					
8	7.49937	3.17E-08	3.36E-17	4.27E-09	7.89E-09	2.38E-08					
9	7.62375	2.38E-08	1.06E-17	1.80E-09	5.89E-09	1.79E-08					
10	7.74739	1.79E-08	3.35E-18	7.65E-10	4.38E-09	1.35E-08					
11	7.86926	1.35E-08	1.05E-18	3.26E-10	3.21E-09	1.03E-08					
12	7.98702	1.03E-08	3.23E-19	1.42E-10	2.28E-09	8.02E-09					
13	8.09557	8.02E-09	9.57E-20	6.41E-11	1.49E-09	6.53E-09					
14	8.18494	6.53E-09	2.55E-20	3.21E-11	7.95E-10	5.74E-09					
15	8.24130	5.74E-09	5.01E-21	2.00E-11	2.51E-10	5.49E-09					
16	8.26069	5.49E-09	4.05E-22	1.68E-11	2.41E-11	5.46E-09					
17	8.26260	5.46E-09	3.50E-24	1.65E-11	2.12E-13	5.46E-09					
18	8.26262	5.46E-09	2.70E-28	1.65E-11	1.64E-17	5.46E-09					
19	8.26262	5.46E-09	0.00E+00	1.65E-11	0.00E+00	5.46E-09					
20	8.26262	5.46E-09	0.00E+00	1.65E-11	0.00E+00	5.46E-09					
21											

Figure 3. Newton's method for pH in carbonate system (CarbonateNewton.XLS)

An alternate approach is to simply create a spreadsheet that computes each equilibrium speciation as a

function of pH, then by trial-and-error choose a pH that satisfies the charge balance. Figure 4 is a

picture of a spreadsheet that does such calculations. The resulting pH =8.2 (basic solution)
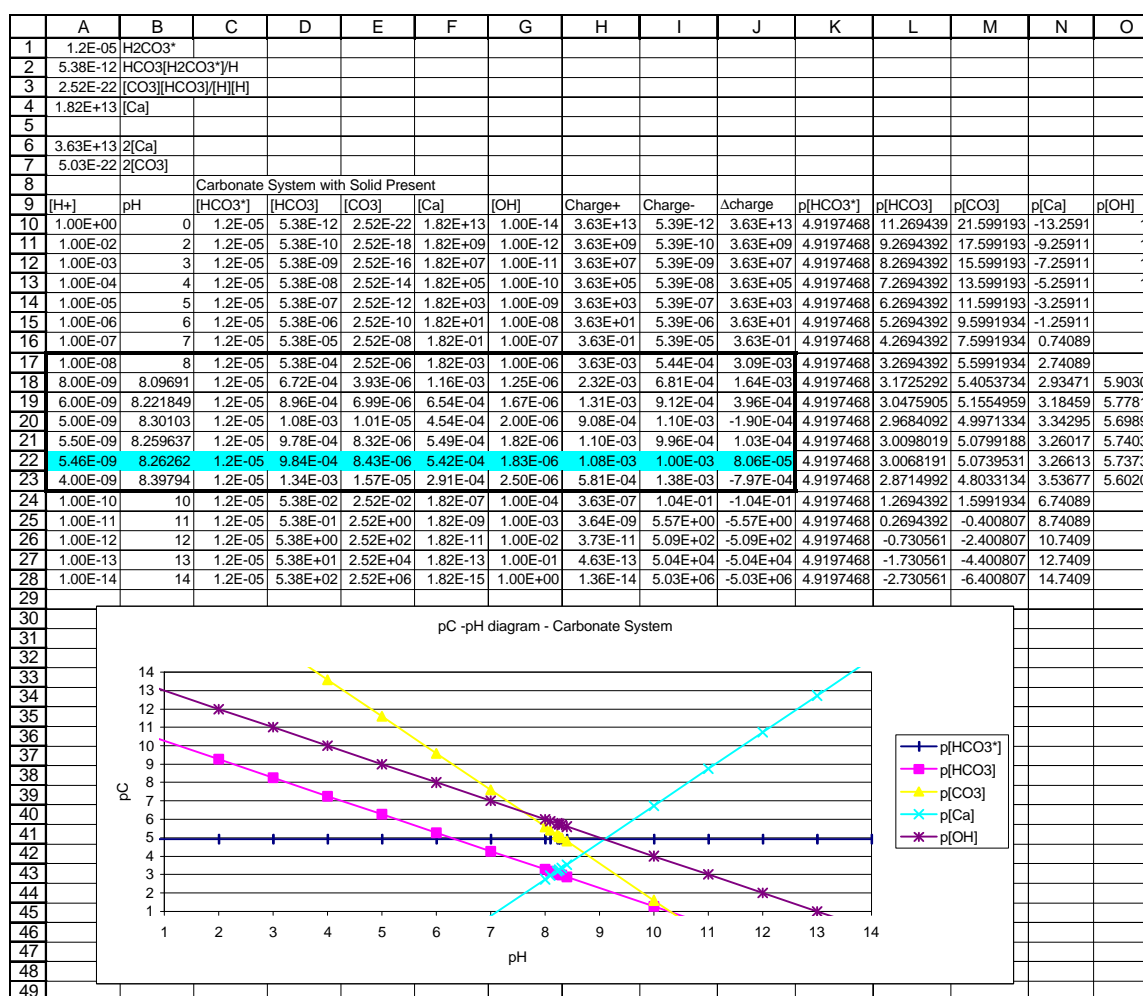
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	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	1.2E-05	H2CO3*													
2	5.38E-12	HCO3[H2CO3*]/H													
3	2.52E-22	[CO3][HCO3]/[H][H]													
4	1.82E+13	[Ca]													
5															
6	3.63E+13	2[Ca]													
7	5.03E-22	2[CO3]													
8			Carbonate System with Solid Present												
9	[H+]	pH	[HCO3*]	[HCO3]	[CO3]	[Ca]	[OH]	Charge+	Charge-	Δcharge	p[HCO3*]	p[HCO3]	p[CO3]	p[Ca]	p[OH]
10	1.00E+00	0	1.2E-05	5.38E-12	2.52E-22	1.82E+13	1.00E-14	3.63E+13	5.39E-12	3.63E+13	4.9197468	11.269439	21.599193	-13.2591	14
11	1.00E-02	2	1.2E-05	5.38E-10	2.52E-18	1.82E+09	1.00E-12	3.63E+09	5.39E-10	3.63E+09	4.9197468	9.2694392	17.599193	-9.25911	12
12	1.00E-03	3	1.2E-05	5.38E-09	2.52E-16	1.82E+07	1.00E-11	3.63E+07	5.39E-09	3.63E+07	4.9197468	8.2694392	15.599193	-7.25911	11
13	1.00E-04	4	1.2E-05	5.38E-08	2.52E-14	1.82E+05	1.00E-10	3.63E+05	5.39E-08	3.63E+05	4.9197468	7.2694392	13.599193	-5.25911	10
14	1.00E-05	5	1.2E-05	5.38E-07	2.52E-12	1.82E+03	1.00E-09	3.63E+03	5.39E-07	3.63E+03	4.9197468	6.2694392	11.599193	-3.25911	9
15	1.00E-06	6	1.2E-05	5.38E-06	2.52E-10	1.82E+01	1.00E-08	3.63E+01	5.39E-06	3.63E+01	4.9197468	5.2694392	9.5991934	-1.25911	8
16	1.00E-07	7	1.2E-05	5.38E-05	2.52E-08	1.82E-01	1.00E-07	3.63E-01	5.39E-05	3.63E-01	4.9197468	4.2694392	7.5991934	0.74089	7
17	1.00E-08	8	1.2E-05	5.38E-04	2.52E-06	1.82E-03	1.00E-06	3.63E-03	5.44E-04	3.09E-03	4.9197468	3.2694392	5.5991934	2.74089	6
18	8.00E-09	8.09691	1.2E-05	6.72E-04	3.93E-06	1.16E-03	1.25E-06	2.32E-03	6.81E-04	1.64E-03	4.9197468	3.1725292	5.4053734	2.93471	5.90309
19	6.00E-09	8.221849	1.2E-05	8.96E-04	6.99E-06	6.54E-04	1.67E-06	1.31E-03	9.12E-04	3.96E-04	4.9197468	3.0475905	5.1554959	3.18459	5.77815
20	5.00E-09	8.30103	1.2E-05	1.08E-03	1.01E-05	4.54E-04	2.00E-06	9.08E-04	1.10E-03	-1.90E-04	4.9197468	2.9684092	4.9971334	3.34295	5.69897
21	5.50E-09	8.259637	1.2E-05	9.78E-04	8.32E-06	5.49E-04	1.82E-06	1.10E-03	9.96E-04	1.03E-04	4.9197468	3.0098019	5.0799188	3.26017	5.74036
22	5.46E-09	8.26262	1.2E-05	9.84E-04	8.43E-06	5.42E-04	1.83E-06	1.08E-03	1.00E-03	8.06E-05	4.9197468	3.0068191	5.0739531	3.26613	5.73738
23	4.00E-09	8.39794	1.2E-05	1.34E-03	1.57E-05	2.91E-04	2.50E-06	5.81E-04	1.38E-03	-7.97E-04	4.9197468	2.8714992	4.8033134	3.53677	5.60206
24	1.00E-10	10	1.2E-05	5.38E-02	2.52E-02	1.82E-07	1.00E-04	3.63E-07	1.04E-01	-1.04E-01	4.9197468	1.2694392	1.5991934	6.74089	4
25	1.00E-11	11	1.2E-05	5.38E-01	2.52E+00	1.82E-09	1.00E-03	3.64E-09	5.57E+00	-5.57E+00	4.9197468	0.2694392	-0.400807	8.74089	3
26	1.00E-12	12	1.2E-05	5.38E+00	2.52E+02	1.82E-11	1.00E-02	3.73E-11	5.09E+02	-5.09E+02	4.9197468	-0.730561	-2.400807	10.7409	2
27	1.00E-13	13	1.2E-05	5.38E+01	2.52E+04	1.82E-13	1.00E-01	4.63E-13	5.04E+04	-5.04E+04	4.9197468	-1.730561	-4.400807	12.7409	1
28	1.00E-14	14	1.2E-05	5.38E+02	2.52E+06	1.82E-15	1.00E+00	1.36E-14	5.03E+06	-5.03E+06	4.9197468	-2.730561	-6.400807	14.7409	0
29															

pC -pH diagram - Carbonate System

Figure 4. Carbonate Equilibria Caclulations - Trial-and-Error

Other carbonate systems of interest: open-system, no solid present. See example in text and Figure 5 below. Methods are same as above except no solid equilibrium. Resulting pH = 5.6 (acidic solution).

Closed system solid present (such as a carbonate aquifer). In such a system a mass balance is required because the total carbon in the system is fixed (there is no atmospheric source after the water percolates into the aquifer). The mass balance used is that the total carbonate in solution must equal the total calcium in solution. In this case one arrives at a result of pH=9.9.
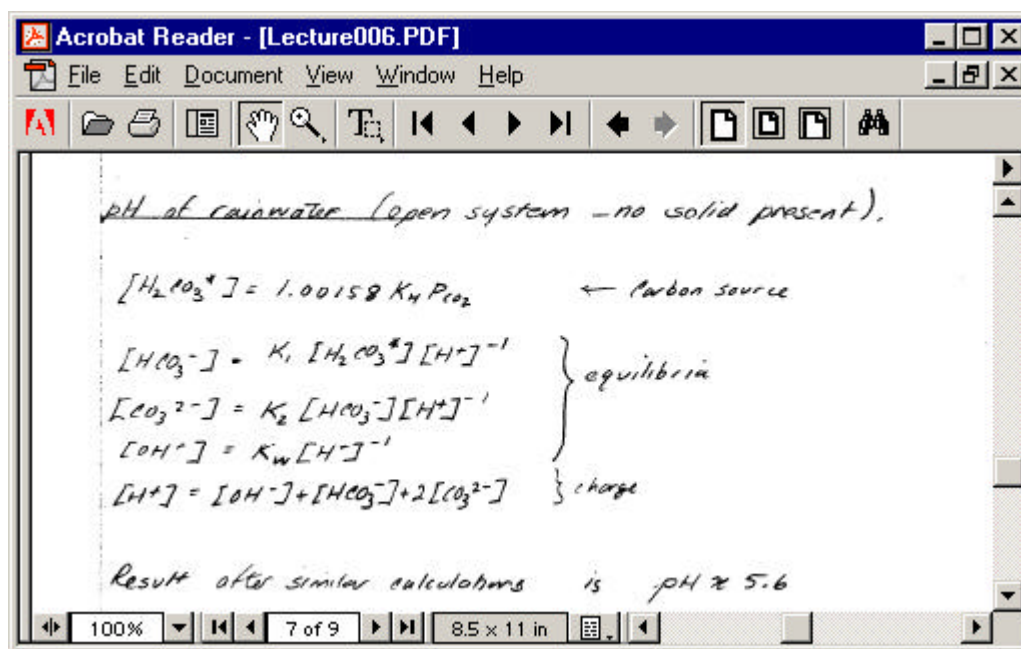
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Figure 5. Equilibria for open-system, no solid

Figure 6 is the sketch of the closed system and Figure 7 are the equilibria for a closed system, with solid present.
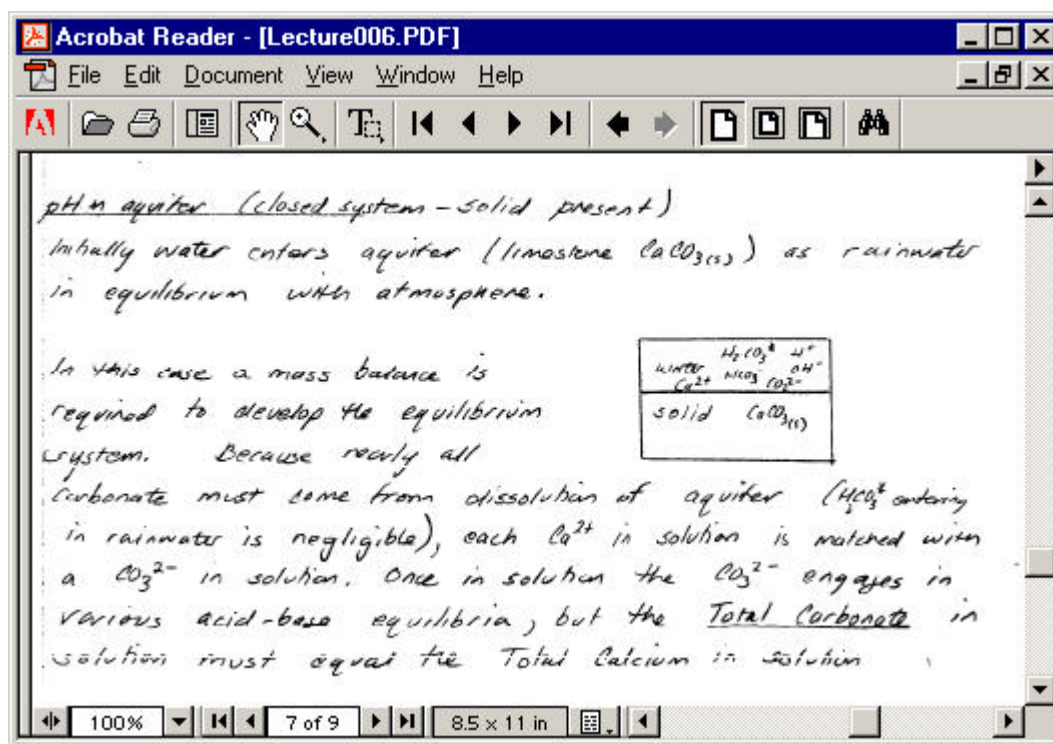
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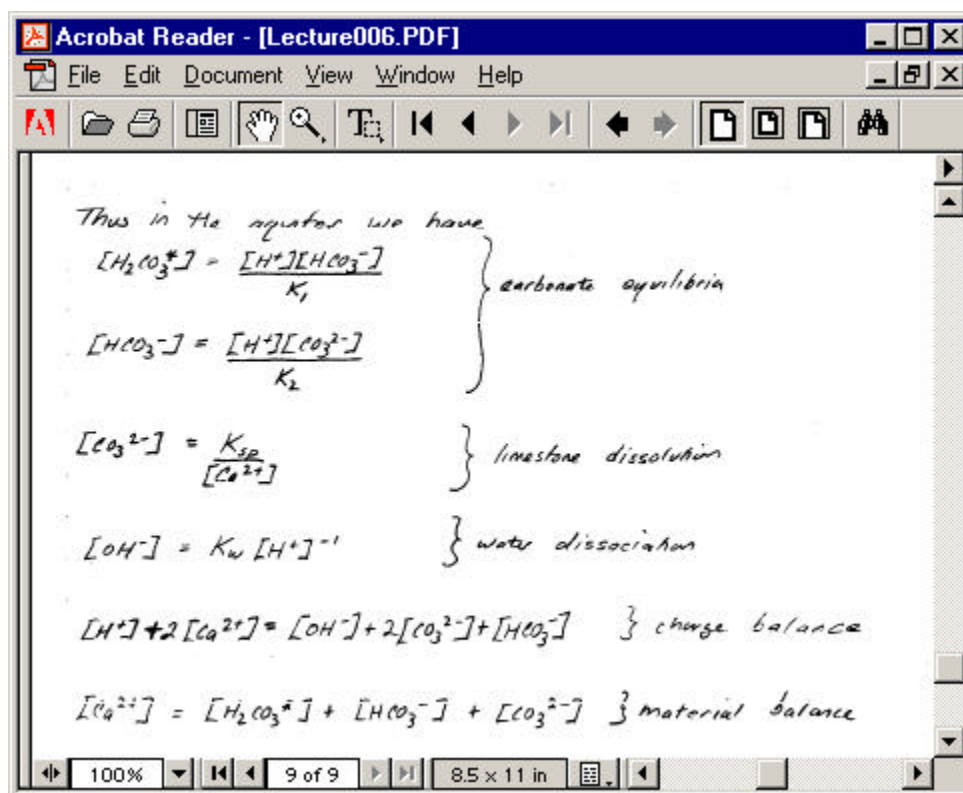**Figure 6. Sketch of closed system with solid**

Figure 7. Equilibria equations for closed system with solid

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