Chapter 12: Acids and Bases: Ocean Carbonate System   **James Murray**
4/30/01   **Univ. Washington**
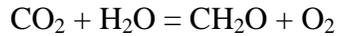
Last lecture was concerned with gas exchange and one example we looked at was the solubility of CO_2. Next we have to ask the question " What happens to the CO_2 that dissolves in water". CO_2 is taken up by ocean biology to produce a flux of organic matter to the deep sea (B_{orgc}). Some carbon is also taken up to make a particulate flux of $CaCO_3$ (B_{CaCO3}). The biologically driven flux is called the "Biological Pump". The sediment record of B_{orgC} and B_{CaCO3} are used to unravel paleoproductivity. The flux of B_{orgC} to sediments drives an extensive set of oxidation-reduction reactions that are part of the diagenesis in marine sediments.
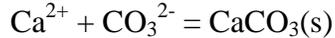
Simple versions of these reactions are:
$$CO_2 + H_2O = CH_2O + O_2$$
and:
$$Ca^{2+} + 2HCO_3^- = CaCO_3(s) + CO_2 + H_2O$$
which can also written as:
$$Ca^{2+} + CO_3^{2-} = CaCO_3(s)$$

The carbonate chemistry controls the pH of seawater which is a master variable for many geochemical processes.
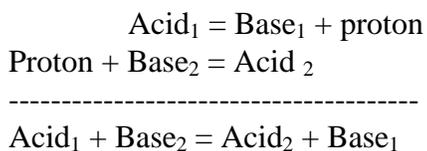
       The species involved in these reactions are $CO_2(g)$, H_2CO_3, HCO_3^- and CO_3^{2-}. What we can measure is a different set of parameters called pH, total CO_2 (also called dissolved inorganic carbon (DIN)), alkalinity and P_{CO2}. We need to learn how to calculate the species we need from the measurements we can make.

First we have to present a general discussion of acids and bases as there are several other acids in seawater besides carbonic acid (H_2CO_3). Then we can discuss the carbonic acid system in more detail.
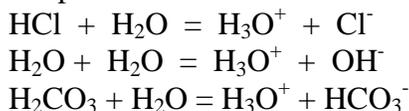
So here goes!

I. Acids and Bases
       Arrhenius (1887) proposed that an acid is a substance whose water solution contained an excess of hydrogen ions. The excess H^+ ions resulted from dissociation of the acid as it was introduced into water. The fact that H^+ ions cannot exist unhydrated in water solution led to the Bronsted Concept in which acids are compounds that can donate a proton to another substance which is a proton acceptor. Thus an acid is considered a proton donor (and a base is a proton acceptor). Proton transfer can only occur if an acid reacts with a base such as:

$$Acid_1 = Base_1 + proton$$
$$Proton + Base_2 = Acid_2$$

$$Acid_1 + Base_2 = Acid_2 + Base_1$$

For example:

$$HCl + H_2O = H_3O^+ + Cl^-$$
$$H_2O + H_2O = H_3O^+ + OH^-$$
$$H_2CO_3 + H_2O = H_3O^+ + HCO_3^-$$

For example, in the first reaction, HCl transfers a proton to H_2O.
Note that water (H_2O), in the second reaction, can be both an acid (proton doner) and a base (proton acceptor).

To simplify this presentation we will write acids as Arrhenius Acids, in which acids simply react to produce excess hydrogen ions in solution. Such as:

$$HCl = H^+ + Cl^-$$

a) Monoprotic Acids

Let's use acetic acid (CH_3COOH) as an example of a monoprotic acid and we will abbreviate it as HA. The base form (CH_3COO^-) will be A^-.

We need to determine the concentrations of 4 species. These are the acid (HA) and base (A^-) forms of acetic acid and H^+ and OH^-. When there are four unknowns we need for equations.

To simplify matters we will neglect activity corrections and assume that activities are equal to concentrations $(\ ) = [\ ]$

The 4 key equations are:

1. The reaction $HA = H^+ + A^-$
           Acid   Hydrogen   Anion (or base)
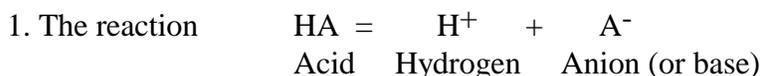
2. Equilibrium Constant $K = (H^+)(A-) / (HA)$ where $(\ )$ = activity
3. Mass balance on A $C_A = [HA] + [A^-]$ (total concentration)
4. Charge Balance $[H^+] = [A^-] + [OH^-]$
(note that the mass and charge balances are written in terms of concentrations not activities.)

pH ($-\log(H^+)$) is used as a master variable (e.g. the parameter against which other concentrations are expressed) for acid-base reactions because it is the variable that determines the distribution of acid and base forms. In addition it is easily measured.

One simple first question is, what is the distribution of the species HA, A^-, H^+ and OH^- as a function of pH?

We need to be able to solve for the concentration of these species. We can do this by two methods. One is algebraic and one is graphical. For illustration these will be done by hand but in practice you would use chemical equilibrium modeling programs like MINEQL+ or HYDRAQL.

b) Algebraic Method

By combining equations 2 and 3 given above we can write algebraic expressions to solve for the main species of acetic acid (HA) and acetate (A$^-$).

$$[HA] = C_T [H^+] / K + H^+$$

$$[A^-] = C_T K / K + H^+$$

The equation for HA is derived using simple algebra as follows:
a. We start with: $K = (H)(A)/(HA)$
b. Rearrange the mass balance to solve for $A = C_T - HA$ and substitute for A in the equilibrium expression.
c. We now have: $K = (H)(C_T - HA) / (HA)$
d. Rearranging this equation gives: $(HA) = (H)C_T / (K + (H))$

The equation for (A) is derived using the same approach but using $HA = C_T - A$ in step b.

For such calculations when you know K and the total concentration (C_T) you can calculate the concentration of HA and A$^-$ for any pH (or H$^+$).

C) Graphical Approach
The approach is to construct a graph or distribution diagram showing how the concentrations of all the species varies with pH. Such graphs are constructed using the equations for HA and A given above. There are three regions for these graphs as discussed below.

Assume:
$K = 10^{-4.7}$ (this is the acidity equilibrium constant for acetic acid, CH_3COOH)

$C_T = 10^{-2}$

$( ) = [ ]$ (e.g. activities equal concentrations, ignore activity corrections to simplify this presentation)

If we make a plot of the concentration of each species as a function of pH there will be three regions

a) $pH = pK$ (e.g. $H^+ = K$)   (this pH is called the system point)

This condition is a point in the diagram. If we look at the equilibrium constant:

$K = (H)(A)/(HA)$

And rearrange it to:

$K / (H) = (A) / (HA)$

We see that when $K = (H)$ the ratio on the left is equal to one and thus:

$[HA] = [A^-] = 1/2 \, C_T$

or in log form:

$\log [HA] = \log [A^-] = \log C_T - \log 2 = \log C_T - 0.3$

b) When $pH \ll pK$ the solution is acidic and $(H^+) > K$

For this condition the algebraic equations for HA and A can be simplified as follows:

$\log [HA] = \log C_T$ (The line for HA has no slope and is equal to C_T)

$\log [A] = \log C_T + \log K - \log H^+$

$= \log C_T + \log K + pH$

$\delta \log [A] / \delta \, pH = +1$ (The line for A has a slope of +1)

c) $pH \gg pK$ (e.g. basic solution, $H^+ \ll K$)

$\log [A-] = \log C_T$

$\log [HA] = \log C_T + \log H^+ - \log K$

$\log C_T - pH - \log K$

$\delta \log [HA] / \delta \, pH = -1$

The steps for constructing the graph are: 1) label axes, 2) draw a horizontal line for total concentration, 3) locate system point, 4) note that the cross over is 0.3 log units below the C_T line, 5) draw lines for the species, 6) draw lines for H^+ and OH^-.

The lines for H^+ and OH^- can be obtained as follows. Write the acidity reaction for H_2O.

$H_2O = H^+ + OH^-$

$K_w = (H^+)(OH^-) / (H_2O)$

$\cong (H^+)(OH^-)$ (because we can assume the activity of pure water solvent is equal to one)

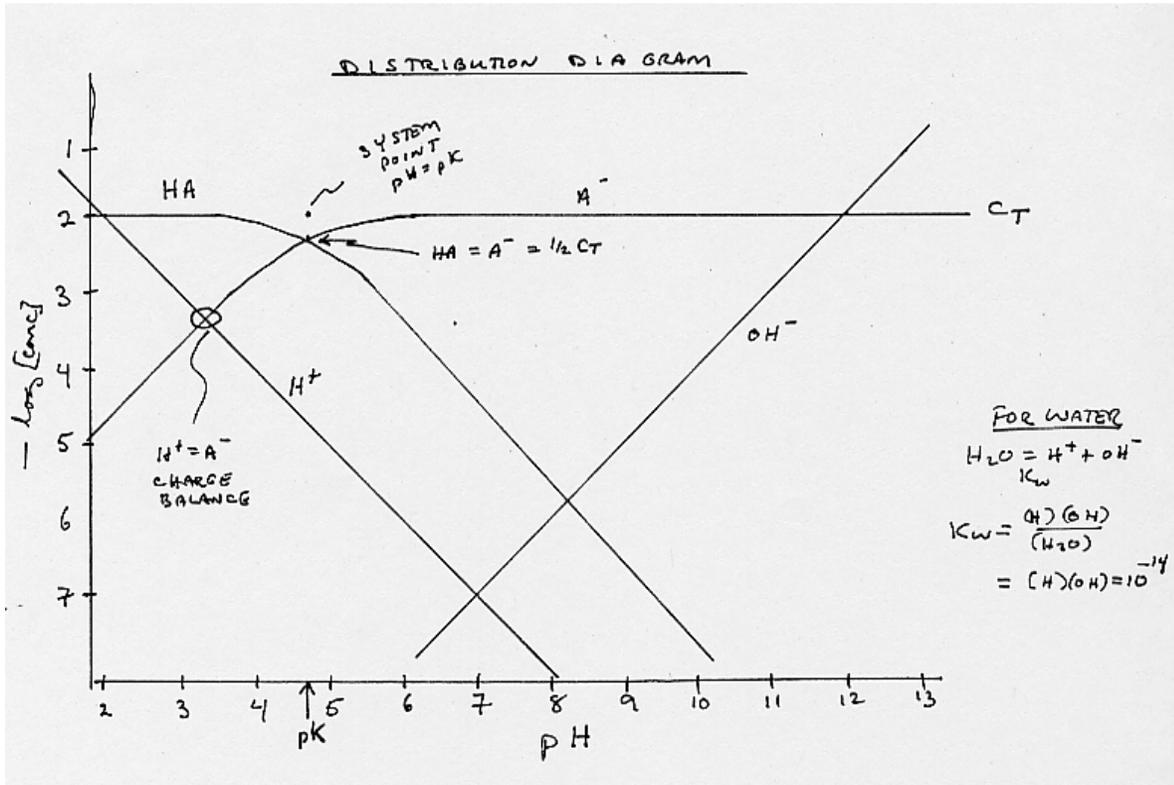The value of $K_w = 10^{-14}$.

Thus:

$\log (H^+) + \log (OH^-) = -14.0$

or

$-pH + -pOH = -14.0$

or

$pH + pOH = 14.0$

Thus at pH = 4.0, the pOH = 10.0

See example on the next page for acetic acid and water (**Fig 12-1**).

Fig. 12-1 Log-log distribution diagram for Acetic Acid showing the distributions of HA, A⁻, H⁺ and OH⁻ as a function of pH.
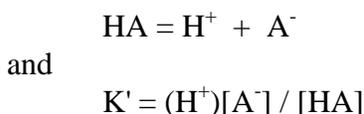
II. Apparent Equilibrium Constants

The difference between concentrations and activities can't be ignored for seawater and chemical oceanographers often use a second approach.

Oceanographers frequently use an equilibrium constant defined in terms of concentrations. These are called apparent or operation equilibrium constants. We use the symbol K' to distinguish them from K. Formally they are equilibrium constants determined on the seawater activity scale.

Apparent equilibrium constants (K') are written in the same form as K except that all species are written as concentrations. The exception is H^+ which is always written as the activity (H^+).

For the monoprotic acid HA we write:

$$HA = H^+ + A^-$$

and

$$K' = (H^+)[A^-] / [HA]$$

The apparent equilibrium constants cannot be calculated from standard free energies of reaction. They have to be determined experimentally in the lab. They must be determined in the same medium or solution to which they will be applied. Thus if we need a value of K' for the acid HA in seawater, someone must have experimentally determined the K for the acidity reaction in a seawater solution with a known salinity (S) at the temperature and pressure of interest. This sounds complicated, and it is. It is a lot of work but fortunately it has been done for several important acids in seawater.

There are pros and cons for both the K and K' approaches.
When we use K the pro is that we can calculate the K from ΔG_r and one value can be used for all problems in all solutions (one K fits all). The cons are that to use K we need to obtain values for the free ion activity coefficients (γ_i) and the %free (f_i) for each solution.

For K' there needs to have been experimental determination of this constant for enough values of S, T and P that equations can be derived to calculate K' for the S, T and P of interest. The good news is that when this has been done the values of K' are usually more precise than the corresponding value of K. The other pro is that we do not need values of γ_i and f_i when we use K'.
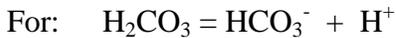
Example 12-1:
The difference between K and K' can be illustrated by this simple example.

$$K = (H^+)(A^-) / (HA) = (H^+)[A^-]\gamma_{T,A^-} / [HA]\, \gamma_{T,HA}$$

Rearrange to get:

$$K = \frac{(H+)\,[A-]}{[HA]}\,\frac{\gamma_{T,A-}}{\gamma_{T,HA}} = K'\,\frac{\gamma_{T,A-}}{\gamma_{T,HA}}$$

You see that the difference in magnitude of K and K' is the ratio of the total activity coefficients of the base to the acid. If you know both K and K' , you can learn something about the activity corrections.

For: $H_2CO_3 = HCO_3^- + H^+$

$$K_1 = (HCO_3^-)(H^+) / (H_2CO_3)$$

or

$$K_1 = \frac{[HCO_3^-]\,\gamma_{T,HCO3}}{[H_2CO_3]\,\gamma_{T,H2CO3}}\,(H^+)$$

or

$$K_1 = \frac{[HCO_3](H^+)\,\gamma_{T,HCO3}}{[H_2CO_3]\,\gamma_{T,H2CO3}} = 10^{-6.3} \quad \text{from tables of } \Delta G_r^\circ \text{ at 25°C and 1 atm}$$

The value of K' has been determined for the same reaction. At S = 35, 25°C and 1 atm

$$K_1' = \frac{[HCO_3^-]\,(H^+)}{[H_2CO_3]} = 10^{-6.0}$$

If we set $K_1 = K_1'\, \gamma_{T,HCO3} / \gamma_{T,\,H2CO3}$

We can solve for $\gamma_{T,HCO3} / \gamma_{T,\,H2CO3} = K_1 / K_1' = 10^{-6.3} / 10^{-6.0} = 10^{-0.3} =$ **5.0 x 10^{-1}**

Example 12-2:
We can compare this ratio with that obtained from the Garrels and Thompson speciation model of surface seawater where:

$$\gamma_{T,HCO3} / \gamma_{T,\,H2CO3} = \frac{f_{HCO3}\,\gamma_{HCO3}}{f_{H2CO3}\,\gamma_{H2CO3}} = \frac{(0.69)(0.68)}{(1.00)(1.13)} = \mathbf{4.1 \times 10^{-1}}$$

Not too bad. Not too good. These two estimates differ by about 20%. Is that good enough?

Table 12-1: The acids of seawater. The concentrations and apparent constants were taken from Edmond (1970). Some elements form more than one acid.

Element	Reaction	mol kg^{-1}	-logC	pK'
H$_2$O	H$_2$O = H$^+$ + OH$^-$			13.9
C	H$_2$CO$_3$ = HCO$_3^-$ + H$^+$	2.4 x 10^{-3}	2.6	6.0
	HCO$_3$- = CO$_3^{2-}$ + H$^+$			9.1
B	B(OH)$_3$ + H$_2$O = B(OH)$_4^-$ + H$^+$	4.25 x 10^{-4}	3.37	8.7
Mg	Mg^{2+} + H$_2$O = MgOH$^+$ + H$^+$	5.32 x 10^{-2}	1.27	12.5
Si	H$_4$SiO$_4$ = SiO(OH)$_3^-$ + H$^+$	1.5 x 10^{-4}	3.82	9.4
P	H$_3$PO$_4$ = H$_2$PO4$^-$ + H$^+$	3.0 x 10-6	5.52	1.6
	H$_2$PO$_4^-$ = HPO$_4^{2-}$ + H$^+$			6.0
	HPO$_4^{2-}$ = PO$_4^{3-}$ + H$^+$			8.6
S(VI)	HSO$_4^-$ = SO$_4^{2-}$ + H$^+$	2.82 x 10^{-2}	1.55	1.5
F	HF = F$^-$ + H$^+$	5.2 x 10^{-5}	4.28	2.5
Ca	Ca^{2+} + H$_2$O = CaOH$^+$ + H$^+$	1.03 x 10-2	1.99	13.0

And in anoxic systems

Element	Reaction	mol kg^{-1}	-logC	pK'
N	NH$_4^+$ = NH$_3$ + H$^+$	10 x 10^{-6}	5.0	9.5
S(-II)	H$_2$S = HS$^-$ + H$^+$	10 x 10^{-6}	5.0	7.0
	HS$^-$ = S^{2-} + H$^+$			13.4

III. Carbonic Acid

Carbonic acid is the classic example of a diprotic acid and it can have a gaseous form. It also can be expressed as open or closed to the atmosphere (or a gas phase)

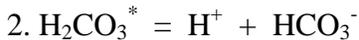There are 6 species we need to solve for:

$CO_2(g)$	Carbon Dioxide Gas
$H_2CO_3^*$	Carbonic Acid ($H_2CO_3^* = CO_2\,(aq) + H_2CO_3$)
HCO_3^-	Bicarbonate
CO_3^{2-}	Carbonate
H^+	Proton
OH^-	Hydroxide

To solve for six unknowns we need six equations.
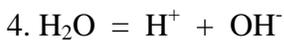Four of these are equilibrium constants. These are writen here as K but could also be expressed as K'.

1. $CO_2(g) + H_2O = H_2CO_3^*$ (Henry's Law)

$K_H = (H_2CO_3^*) / P_{CO2}$ (note that gas concentrations are given as partial pressure; e.g. atmospheric $P_{CO2} = 10^{-3.5}$)

2. $H_2CO_3^* = H^+ + HCO_3^-$

$K_1 = (HCO_3^-)(H^+) / H_2CO_3^*)$

3. $HCO_3^- = H^+ + CO_3^{2-}$

$K_2 = (H^+)(CO_3^{2-}) / (HCO_3^-)$

4. $H_2O = H^+ + OH^-$
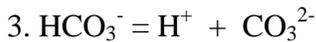
$K_w = (H^+)(OH^-)$

Representative values for these constants are given below. Equations are given in Millero (1995) with which you can calculate all K's for any salinity and T, P conditions. The values here are for S = 35, 25°C and 1 atm.

Constant	Thermodynamic Constant (K)	Apparent Seawater Constant (K')
K_H	$10^{-1.47}$	$10^{-1.53}$
K_1	$10^{-6.35}$	$10^{-6.00}$
K_2	$10^{-10.33}$	$10^{-9.10}$
K_w	$10^{-14.0}$	$10^{-13.9}$

We can also define total CO_2 (also referred to as DIC, C_T or ΣCO_2)

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

IV. Construct a Distribution Diagram for H_2CO_3

a. First specify the total CO_2 (e.g. $C_T = 2.0 \times 10^{-3} = 10^{-2.7}$ M)
b. Locate C_T on the graph and draw a horizontal line for that value.
c. Locate the two system points on that line where $pH = pK_1$ and $pH = pK_2$.
d. Make the crossover point, which is 0.3 log units less than C_T
e. Sketch the lines for the species.

Boric Acid $(B(OH)_3)$ is another important acid is seawater (Table 12-1). Draw it on the graph as well.
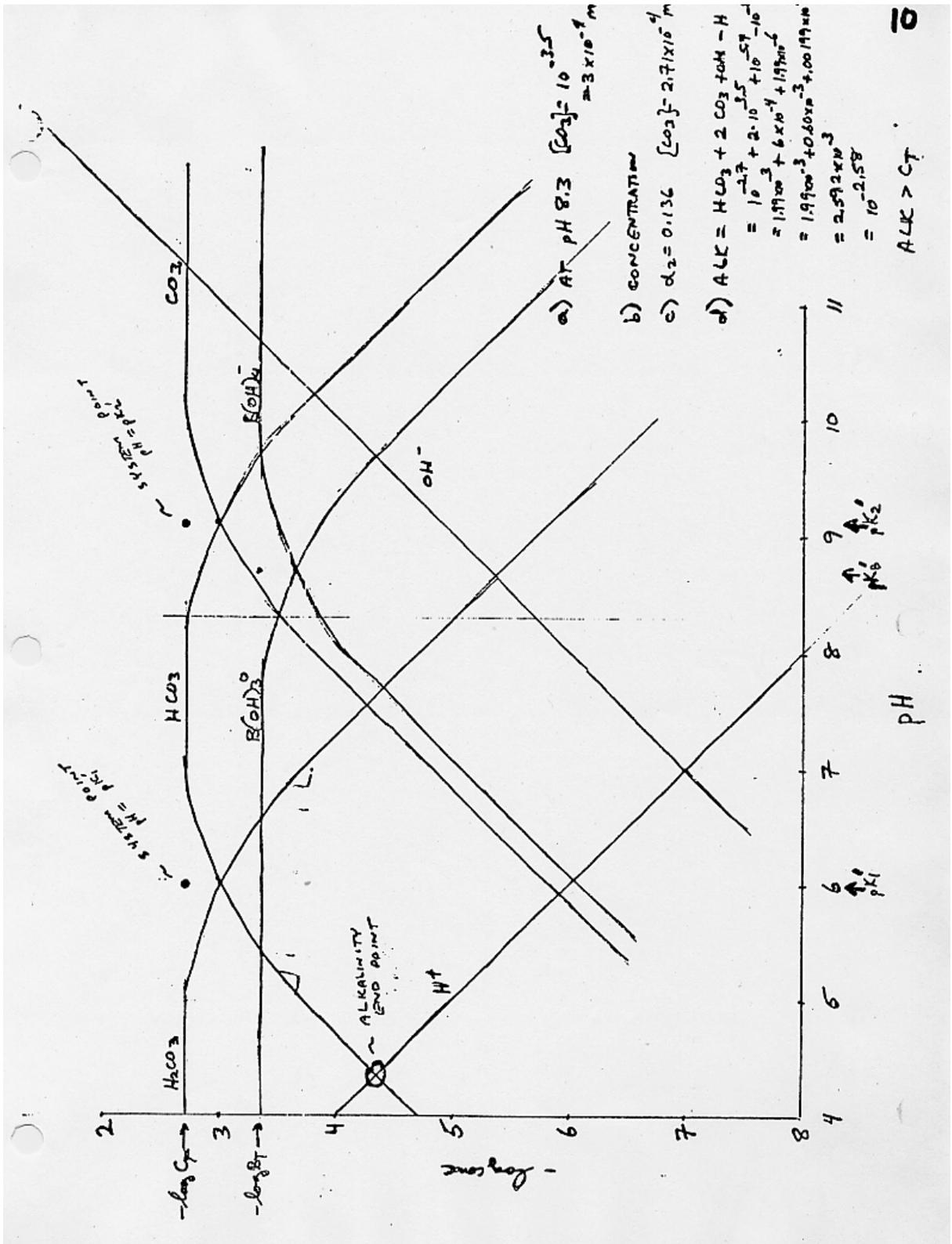
Use $B_T = 10^{-3.3} = 5.0 \times 10^{-4}$ M and $K_B' = 10^{-8.7}$

With this graph you can locate the concentration of any of the required species at any pH.

The graph is shown in **Fig 12-2**.

At the pH of surface seawater (about pH 8.3) the main species is HCO_3^-. CO_3^{2-} is next followed by H_2CO_3.

Fig 12-2 Log-log distribution diagram of carbonic acid and boric acid in seawater.

a) AT pH 8.3 $[CO_3]= 10^{-3.5}$
$= 3 \times 10^{-4} m$

b) CONCENTRATION

c) $d_2 = 0.136$ $[CO_3] = 2.7 \times 10^{-4} m$

d) $ALK = HCO_3 + 2 CO_3 + OH - H$
$= 10^{-2.7} + 2 \cdot 10^{-3.5} + 10^{-5.7} - 10^{-10}$
$= 1.99 \times 10^{-3} + 6 \times 10^{-4} + 1.99 \times 10^{-6}$
$= 1.99 \times 10^{-3} + 0.60 \times 10^{-3} + 1.00199 \times 10^{-6}$
$= 2.592 \times 10^{-3}$
$= 10^{-2.58}$

$ALK > C_T$

CO_3

$B(OH)_4^-$

OH^-

HCO_3^-

$B(OH)_3^0$

H^+

H_2CO_3

$\sim$ SYSTEM pH = $\frac{1}{2} pK_2$ POINT

$\sim$ SYSTEM pH = $\frac{1}{2} pK_1$ POINT

ALKALINITY END POINT

$-\log C_T \rightarrow$

$-\log B_T \rightarrow$

$-\log conc$

2
3
4
5
6
7
8

pH

4   6   7 $\underset{pK_1}{\uparrow}$ 8   9 $\underset{pK_b pK_2}{\uparrow\uparrow}$ 10   11

$\underset{pK_1^o}{\uparrow}$ $\underset{pK_b^o pK_2^o}{\uparrow}$

10

V. Carbonate System Measurements

For our calculations, such as CO_2 gas exchange or $CaCO_3$ solubility, we want the concentrations of H_2CO_3 or CO_3^{2-}. We can not measure these species directly. The four parameters that can be measured are pH, Total CO_2, Alkalinity and P_{CO2}.

a) pH

pH is defined in terms of the activity of H^+ or as pH = -log (H^+) = -log γ_H[H+}

The historical approach was to measure pH using a glass electrode calibrated with buffer solutions prepared by the National Bureau of Standards. This is called the NBS Scale. The NBS has now become the NIST. Thought the precisioon can be quite good (±0.003) the accuracy is no better than about ±0.02 because of several factors including the liquid junction potential and the assumption of a single ion activity coefficient.

New colorimetric methods have been developed where the ratio of the acid and base form of a H^+ sensitive dye are measured. For example pH dependent reaction between the acid and base forms of sulfonephthalein dyes such as phenol red and bromocresol green (Byrne et al, 1988) and cresol red (Byrne and Breland, 1989) can be written as:

$$HL^- = L^{2-} + H^+$$
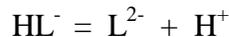
The relative concentrations of the acid and base forms are related to pH through the equation:

$$pH = pK_2 + log\ [L^{2-}]/[HL^-]$$

Each form absorbs light at a different wavelength. Either single or double wavelength approaches can be used but the multiple wavelength approach is more precise.

The calculation is then of pH on the total H scale and on the seawater scale. These are written as:

$$pH_T = -log[H^+]_T = -log\{[H^+] + [HSO_4^-]\}$$

and

$$pH_{sws} = -log[H_{sws}] = -log\{[H^+] + [HSO_4^-] + [F^-]\}$$

See Millero (1995) for discussion and references.

b) Total CO_2

Total CO_2 (expessed as C_T or DIC or ΣCO_2) is defined as the sum of the concentrations of the three carbonate species:

$$C_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

It is determined by acidifying a seawater sample to about pH 2. This converts all the carbonate species to H_2CO_3, which is essentially equivalent to $CO_2(aq)$, which can be driven off with an inert carrier gas (e.g. He) and analyzed with an infrared (IR) detector.

c) Alkalinity

Alkalinity = $[HCO_3^-]$ + $2[CO_3^{2-}]$ + $[OH^-]$ - $[H^+]$ + $[B(OH)_4^-]$ + any other bases present such as $[SiO(OH)_3^-]$, $[HS^-]$, $[NH_3]$ and $[MgOH^+]$.

The alkalinity is defined as the amount of acid necessary to titrate all the weak bases in seawater (e.g. HCO_3^-, CO_3^{2-}, $B(OH)_4^-$) to the alkalinaity endpoint which occurs where (H^+) = (HCO_3^-). This point is circled in **Fig 12-2** and occurs at about pH = 4.3. At this pH all the carbonate species (HCO_3^- and CO_3^{2-}) have been converted to H_2CO_3. It is determined using an acid titration. The data are treated by a procedure called the Gran Plot.

The concentration is expressed as equivalents kg^{-1} , rather than moles kg^{-1}, because each species is multiplied by the number of protons it consumes. For example, when acid is added HCO_3^- consumes two protons as it is converted to H_2CO_3. CO_3^{2-} consumes two protons, thus its concentration is multiplied by two.

$$HCO_3^- + H^+ \rightarrow H_2CO_3$$
$$CO_3^{2-} \ + \ 2H^+ \rightarrow H_2CO_3$$
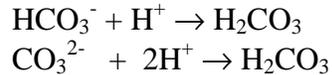
An acid titration is blind to the identity of the base (as long as its pK > pK_1 for carbonic acid) thus all weak acids present in seawater are titrated. Borate is the most important of these.

$$B(OH)_4^- \ + \ H^+ \rightarrow \ B(OH)_3^\circ$$

d) P$_{CO2}$

The P_{CO2} in a sample is the P_{CO2} that a water would have if it were in equilibrium with a gas phase. It is determined by equilibrating a known volume of water with a known volume of gas and measuring the CO_2 in the gas phase, again by IR detection.

VI. Ocean Distributions

Examples of the vertical distributions of pH, C_T, Alkalinity and P_{CO2} for the North Atlantic (25°W; 27°N) and North Pacific (110°W; 16°N) are shown in **Fig 12-3**. There are many observations we can make about these profiles. (R. Feely, personal communication).

pH - The surface values in both oceans are just slightly higher than pH = 8.1. This is close to the value expected for water of seawater alkalinity in equilibium with the atmosphere with $P_{CO2} = 10^{-3.5}$. pH then decreases to a minimum in both oceans, however the minimum is much more intense in the Pacific (to about pH = 7.3) than the Atlantic (pH = 7.75). The depth of this pH minimum corresponds to the depth of the oxygen minimum (not shown). In the deep sea the pH increases slowly, but at all depths the pH in the Pacific (pH ≈ 7.5) is less than that in the Atlantic (pH ≈ 7.8).

DIC - The total CO_2 is about 1950 μmol kg^{-1} in the surface Atlantic and Pacific. It then increases with depth. The increase is steep in the upper 1000m and then is more gradual in the deeper water. All subsurface DIC concentrations in the deep Pacific (about 2350 μmol kg^{-1}) are higher than in the deep Atlantic (about 2200 μmol kg^{-1}).

Alkalinity - The values plotted here are for total alkalinity so it includes the concentrations of all titratable bases. Alkalinity in the surface Atlantic is about 2300 μeq kg^{-1}, while the surface Pacific is slightly lower at 2250 μeq kg^{-1}. Alkalinaity increases less steeply than does DIC. The deep values are higher in the Atlantic (2350 μeq kg^{-1}) than the Pacific (2425 μeq kg^{-1}).

P_{CO2} - In most regards the distribution of P_{CO2} is a mirror image of pH. When pH goes down, P_{CO2} goes up. The surface values in both ocean are about 350 μatm, which is about the value of the atmosphere. P_{CO2} increases to a maximum of about 800 μatm in the Atlantic but over 2000 μatm in the Pacific.

Fig 12-3
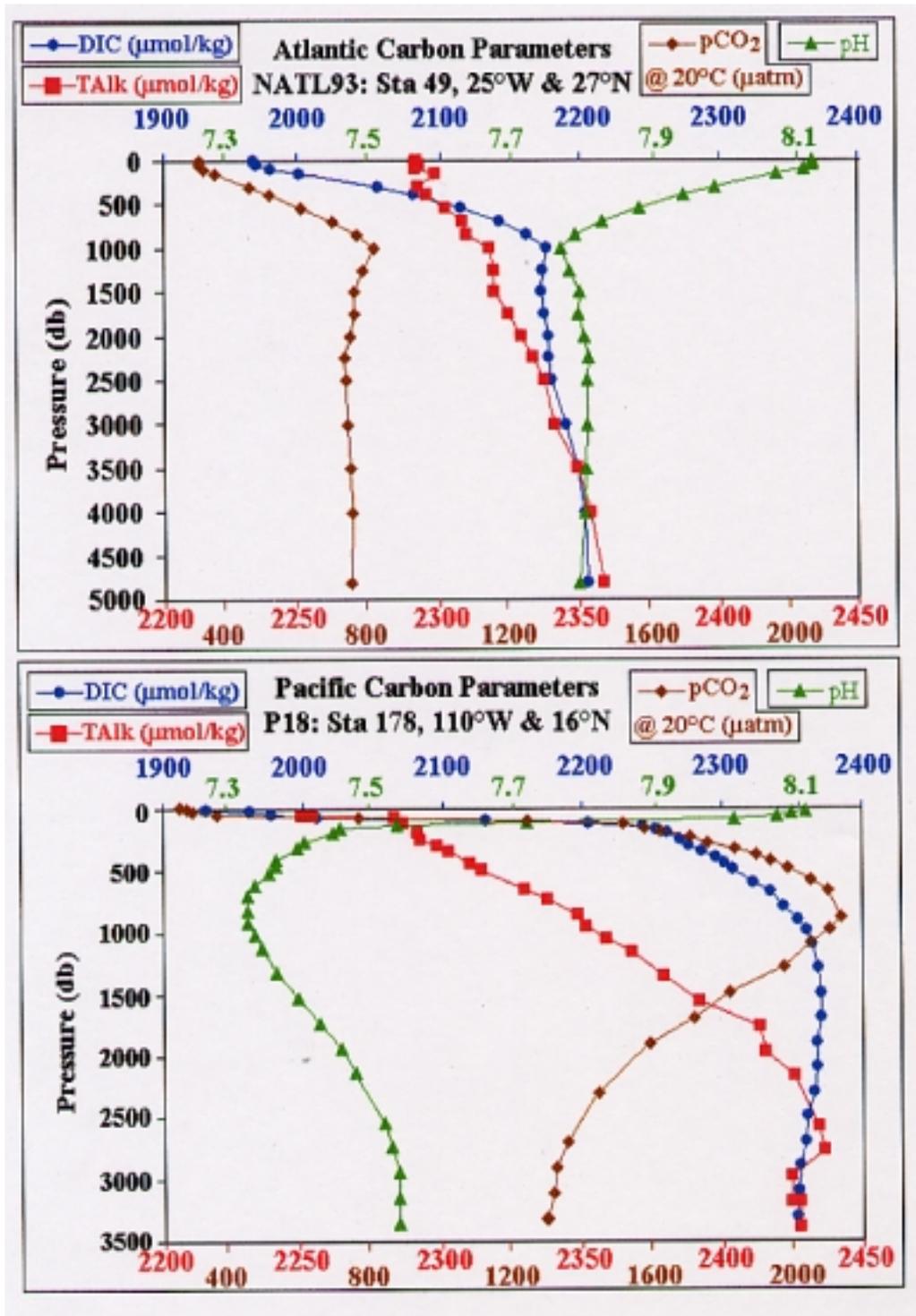
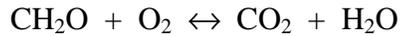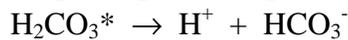## VII. Controls on ocean distributions.

A) Photosynthesis/Respiration

Organic matter (approximated as CH_2O for this example) is produced and consumed as follows:

$$CH_2O + O_2 \leftrightarrow CO_2 + H_2O$$

Then:

$$CO_2 + H_2O \rightarrow H_2CO_3*$$
$$H_2CO_3* \rightarrow H^+ + HCO_3^-$$
$$HCO_3^- \rightarrow H^+ + CO_3^{2-}$$

As CO_2 is produced during respiration we should observe:

$$pH \downarrow \quad DIC \uparrow \quad Alk \leftrightarrow \quad P_{CO2} \uparrow$$

The trends will be the opposite for photosynthesis.

B) $CaCO_3$ dissolution/precipitation

$$CaCO_3(s) \leftrightarrow Ca2+ + CO_3^{2-}$$
Also written as:
$$CaCO_3(s) + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2 HCO_3^-$$
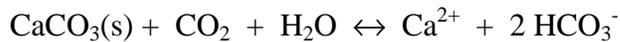
As $CaCO_3(s)$ dissolves, CO_3^{2-} is added to solution. We should observe:

$$pH \uparrow \quad DIC \uparrow \quad Alk \uparrow \quad P_{CO2} \downarrow$$

The trends pedicted by these processes can be seen in the 6 vector diagrams in **Fig 12-4** (from Park, 1969). Here AOU and carbonate dissolution vectors are plotted for the same initial conditions for 6 different pairs of variables. The dots represent sequential additions of DIC = 0.050 mM by either respiration (expressed as AOU) or carbonate dissolution. The initial values were Alk = 2487 μeq kg^{-1}, pH = 8.200 and DIC = 2300 μmol kg^{-1}.
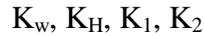
Fig 12-4
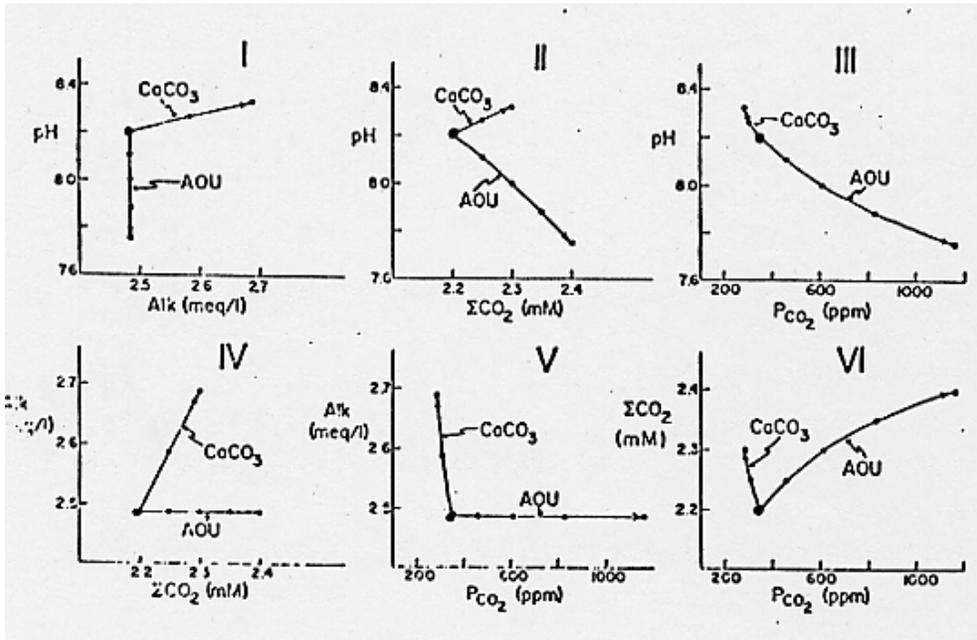
VIII. Carbonate system calculations

Unknowns:

P_{CO2}, $H_2CO_3^*$, HCO_3^-, CO_3^{2-}, H^+, OH^-

Equations:

K_w, K_H, K_1, K_2

Analyze two of the following:

P_{CO2}, Alk, DIC, pH

Equations can be derived to solve for each species in terms of two of these variables. See the pass out from Dickson (1994)

Here we will show examples for the following.

pH and Alkalinity
pH and DIC
pH and P_{CO2}
Alk and DIC

Example 1: Measure pH and DIC (or C_T)

A useful shorthand is the alpha notation, where the alpha (α) express the fraction each carbonate species is of the total DIC. These α values are a function of pH only for a given set of acidity constants. Thus:

$H_2CO_3 = \alpha_0 \ C_T$
$HCO_3^- = \alpha_1 \ C_T$
$CO_3^{2-} = \alpha_2 \ C_T$
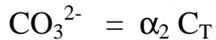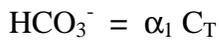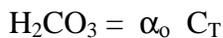
The derivations of the equations are as follows:

$\alpha_0 = H2CO3 / CT = H_2CO_3 \ / \ (H_2CO_3 + HCO_3 + CO_3)$
$= 1 \ / \ (1 + HCO_3/H_2CO_3 \ + \ CO_3/H_2CO_3)$
$= 1 \ / \ (1 + K_1/H \ + \ K_1K_2/H^2)$
$= H^2 \ / \ (H^2 \ + \ HK_1 \ + \ K_1K_2)$

The values for α_1 and α_2 can be derived in a similar manner.

$\alpha_1 = HK_1 / (H^2 + H K_1 + K_1K_2)$

$\alpha_2 = K_1K_2 / (H^2 + H K_1 + K_1K_2)$

For example:

Assume pH = 8, DIC = 10^{-3}, $pK_1' = 6.0$ and $pK_2' = 9.0$

$[H_2CO_3*] = 10^{-5}$ mol kg^{-1}

(note the answer is in concentration becasue we used K')

$[HCO_3^-] = 10^{-3}$ mol kg^{-1}

$[CO_3^{2-}] = 10^{-4}$ mol kg^{-1}

Example 2: An open system problem where we know alkalinity and P_{CO2}. What is the pH?

Alk $\quad = HCO_3 + 2 CO_3 + OH - H$

For this problem neglect H and OH (a good assumption), then:

$\qquad = C_T \alpha_1 + 2 C_T \alpha_2$

$\qquad = C_T (\alpha_1 + 2\alpha_2)$

We can use this equation if we have a closed system and we know 2 of the 3 variables (Alk, C_T or pH).

For an open system we can express C_T in terms of P_{CO2} as follows:

We know that $H_2CO_3* = C_T \alpha_o$ (you can also use this equation if you know pH and P_{CO2})

But H_2CO_3 can be expressed in terms of the Henry's Law:

$\qquad\qquad K_H P_{CO2} = C_T \alpha o$

$\qquad\qquad$ So

$\qquad\qquad C_T = K_H P_{CO2} / \alpha o$

Now:

$$\text{Alk} = (K_H \, P_{CO2} \, / \, \alpha o \,) \, (\; \alpha_1 \; + \; 2\alpha_2)$$

$$\text{Alk} = K_H \, P_{CO2} \; (\; (\alpha_1 + \; 2 \; \alpha_2 \,) \, / \, \alpha_o \,)$$

$$\text{Alk} = K_H \, P_{CO2} \; (\; HK_1 \; + \; 2 \, K_1 K_2 \, / \, H^2 \,)$$

Assume:

$$\text{Alk} = 10^{-3}$$
$$P_{CO2} = 10^{-3.5}$$
$$pK_1' = 6.0$$
$$pK_2' = 9.0$$

Then: pH = 8.3

Problems:
1. How will fossil fuel CO_2 change the pH of the ocean?
Scientists project that P_{CO2} will eventually double from its pre-industrial value of 280 ppm to at least 600 ppm. Assume alkalinity stays constant at 2.300 x 10^{-3} eq l^{-1}.
Assume $K_1' = 10^{-6.0}$ and $K_2' = 10^{-9.1}$

a. What are the pros and cons regarding the asumption that the alkalinity stays constant?
b. What will be the final pH for this model?

2. The deep water of the Black Sea does not get replenished very often thus dissolved oxygen is absent and hydrogen sulfide is very high.

a. What is the sulfide (S^{2-}) concentration in the deep water of the Black Sea. Use the graphical or algebraic approach (your choice). If you use the graphical approach, paper is attached.(10 points)
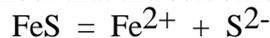
    Total sulfide (S_T) equals 400 µM
    pH is 7.7
    There are two apparent acidity constants for H_2S in seawater:
$$K_1' = 10^{-7} \text{ and } K_2' = 10^{-14}$$
b. Is iron sulfide (FeS_{am}) supersaturated? (10 points)
    Remember that the solubility reaction is:
$$FeS \; = \; Fe^{2+} \; + \; S^{2-}$$
    and the apparent solubility constant in seawater is:
$$K_{sp}' = 10^{-19}$$
The concentration of Fe^{2+} is 200 nM

3. As a result of $CaCO_3$ precipitation:

a. P_{CO_2} goes down
b. pH goes up
c. P_{CO2} goes down
d. Alkalinity stays constant

4.. Many of the Lakes in New England have become acidified due to industrial emissions. The pH of one such lake is 5.2. In descending order of concentration, the inorganic carbon speciation in this lake would be:

a. H_2CO_3, HCO_3^-, CO_3^{2-}
b. HCO_3^-, CO_3^{2-}, H_2CO_3
c. CO_3^{2-}, HCO_3^-, H_2CO_3
d. HCO_3^-, H_2CO_3, CO_3^{2-}

5. The deep water of the Black Sea does not get replenished very often thus dissolved oxygen is absent and the concentration of phosphate is very high. It has been hypothesized that iron phosphate compounds precipitate just below the oxic-anoxic interface and this influences phosphate cycling in that region of the water column.

a. What is the phosphate ion (PO_4^{3-}) concentration in the anoxic water of the Black Sea. Use the graphical or algebraic approach (your choice). If you use the graphical approach, paper is attached.(20 points)
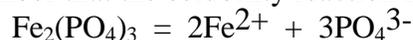
Total phosphate (P_T) equals 5 μM
pH is 7.7
There are three apparent acidity constants for H_3PO_4 in seawater:

$$K_1' = 10^{-1.6}\;;\;\; K_2' = 10^{-6.0}\;\;\text{and } K_3' = 10^{-8.6}$$

b. Is ferrous iron phosphate$(Fe_2(PO_4)_3(s))$ supersaturated? (20 points)
Remember that the solubility reaction is written as:
$$Fe_2(PO_4)_3 = 2Fe^{2+} + 3PO_4^{3-}$$
where the thermodynamic solubility constant (infinite dilution value) is:
$$Kso = 10^{-36.0}$$
The total concentration of dissolved iron (Fe_T) is 100 nM $(100 \times 10^{-9}$ M)
Explain clearly the assumptions you make for estimating activity corrections.

References

Edmond J. (1970) Deep-Sea Research, 17, 737-750

Lewis E. and D. Wallace (1998) Program developed for the CO2 system calculations. Web Site: http://cdiac.esd.ornl.gov/ftp/co2sys.

Millero F.J. (1995) Thermodynamics of the carbon dioxide system in the oceans. Geochimica et Cosmochimica Acta, 59, 661-677.