

# Carbonate equilibria in natural waters

A Chem1 Reference Text

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Natural waters, which include the ocean and freshwater lakes, ponds and streams, act as a major interface between the lithosphere and the atmosphere, and also between these environmental compartments and much of the biosphere. In particular the ocean, with its large volume, serves as both a major reservoir for a number of chemical species; the deep ocean currents also provide an efficient mechanism for the long distance transport of substances.

Although it is commonly stated that the composition of natural waters is controlled by a combination of geochemical and biological processes, it is also true that these processes are to some extent affected by the composition of the waters. Among the parameters of water composition, few are more important than the pH and the alkalinity. The latter affects the degree to which waters are buffered against changes in the pH, and it also has some influence on the complexing of certain trace cations.

Natural waters contain a variety of weak acids and bases which include the major elements present in living organisms. By far the most important of these is carbon in the form of  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ . The carbonate system which is the major source of buffering in the ocean and is the main subject of this chapter. The carbonate system encompasses virtually all of the environmental compartments— the atmosphere, hydrosphere, biosphere, and, as  $\text{CaCO}_3$ , major parts of the lithosphere. The complementary processes of photosynthesis and respiration drive a global cycle in which carbon passes slowly between the atmosphere and the lithosphere, and more rapidly between the atmosphere and the oceans.

base	fresh water	warm surface	deep Atlantic	deep Pacific
carbonate	970	2100	2300	2500
silicate	220	< 3	30	150
ammonia	0-10	< 500	< 500	< 500
phosphate	0.7	< .2	1.7	2.5
borate	1	0.4	0.4	0.4

Table 1: Buffering systems present in natural waters,  $\mu M$

<i>source</i>	<i>moles C × 10<sup>18</sup></i>	<i>relative to atmosphere</i>
<b>sediments</b>		
carbonate	1530	28,500
organic carbon	572	10,600
<b>land</b>		
organic carbon	.065	1.22
<b>ocean</b>		
CO <sub>2</sub> + H <sub>2</sub> CO <sub>3</sub>	.018	0.3
HCO <sub>3</sub> <sup>-</sup>	2.6	48.7
CO <sub>3</sub> <sup>2-</sup>	.33	6.0
dead organic	.23	4.4
living organic	.0007	.01
<b>atmosphere</b>		
CO <sub>2</sub>	.0535	<b>1.0</b>

Table 2: Distribution of carbon on the Earth.

## 1 Carbon dioxide in the atmosphere

CO<sub>2</sub> has probably always been present in the atmosphere in the relatively small absolute amounts now observed. Precambrian limestones, possibly formed by reactions with rock-forming silicates, e.g.



have likely had a moderating influence on the CO<sub>2</sub> abundance throughout geological time.

The volume-percent of CO<sub>2</sub> in dry air is .032%, leading to a partial pressure of  $3 \times 10^{-4}$  ( $10^{-3.5}$ ) atm. In a crowded and poorly-ventilated room,  $P_{\text{CO}_2}$  can be as high as  $100 \times 10^{-4}$  atm.

About 54E14 moles per year of CO<sub>2</sub> is taken from the atmosphere by photosynthesis divided about equally between land and sea. Of this, all except .05% is returned by respiration (almost entirely due to microorganisms); the remainder leaks into the slow, sedimentary part of the geochemical cycle.

Since the advent of large-scale industrialization around 1860, the amount of CO<sub>2</sub> in the atmosphere has been increasing. Most of this has been due to fossil-fuel combustion; in 1966, about 3.6E15 g of C was released to the atmosphere, which is about 12 times greater than the estimated natural removal of carbon into sediments. The large-scale destruction of tropical forests, which has accelerated greatly in recent years, is believed to exacerbate this effect by removing a temporary sink for CO<sub>2</sub>.

About 30-50% of the CO<sub>2</sub> released into the atmosphere by combustion remains there; the remainder enters the hydrosphere and biosphere. The oceans have a large absorptive capacity for CO<sub>2</sub> by virtue of its transformation into bicarbonate and carbonate in a slightly alkaline aqueous medium, and they contain about 60 times as much inorganic carbon as is in the atmosphere. However, efficient transfer takes place only into the topmost (100 m) wind-mixed layer, which contains only about one atmosphere equivalent of CO<sub>2</sub>; mixing time into the deeper parts of the ocean is of the order of 1000 years. For this reason, only about ten percent of the CO<sub>2</sub> added to the atmosphere is taken up by the oceans.

## 2 The carbonate system in aqueous solution

By “carbonate system” we mean the set of species produced by the equilibria



temperature	p <i>K</i> H	p <i>K</i> <sub>1</sub>	p <i>K</i> <sub>2</sub>	p <i>K</i> <sub>w</sub>
<i>fresh water</i> 5 °C	1.19	6.517	10.56	14.73
	<b>25</b>	<b>1.47</b>	<b>6.35</b>	<b>10.33</b>
	50	1.72	6.28	10.17
<i>seawater</i> 25 °C	1.54	5.86	8.95	13.20

Table 3: Some concentration equilibrium constants relating to CO<sub>2</sub> equilibria

In this section we will examine solutions of carbon dioxide, sodium bicarbonate and sodium carbonate in pure water. The latter two substances correspond, of course, to the titration of H<sub>2</sub>CO<sub>3</sub> to its first and second equivalence points.

## 2.1 Carbon dioxide in aqueous solution

Carbon dioxide is slightly soluble in pure water; as with all gases, the solubility decreases with temperature:

0 °C	4 °C	10 °C	20 °C	
.077	.066	.054	.039	mol/litre

At pressures up to about 5 atm, the solubility follows Henry’s law

$$[\text{CO}_2] = K_{\text{H}}P_{\text{CO}_2} = .032P_{\text{CO}_2} \quad (2)$$

Once it has dissolved, a small proportion of the CO<sub>2</sub> reacts with water to form carbonic acid:

$$[\text{CO}_2(aq)] = 650 [\text{H}_2\text{CO}_3] \quad (3)$$

Thus what we usually refer to as “dissolved carbon dioxide” consists mostly of the hydrated oxide CO<sub>2</sub>(aq) together with a small amount of carbonic acid<sup>1</sup> When it is necessary to distinguish between “true” H<sub>2</sub>CO<sub>3</sub> and the equilibrium mixture, the latter is designated by H<sub>2</sub>CO<sub>3</sub>\*<sup>2</sup>.

Water exposed to the atmosphere with  $P_{\text{CO}_2} = 10^{-3.5}$  atm will take up carbon dioxide until, from Eq 2,

$$[\text{H}_2\text{CO}_3^*] = 10^{-1.5} \times 10^{-3.5} = 10^{-5} \text{ M} \quad (4)$$

The following equilibria are established in any carbonate-containing solution:

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} = K_1 = 10^{-6.3} \quad (5)$$

$$\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_2 = 10^{-10.3} \quad (6)$$

$$[\text{H}^+][\text{OH}^-] = K_w \quad (7)$$

$$C_{\text{T}} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (\text{mass balance}) \quad (8)$$

$$[\text{H}^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-] = 0 \quad (\text{charge balance}) \quad (9)$$

<sup>1</sup>Unlike proton exchange equilibria which are kinetically among the fastest reactions known, the interconversion between CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub>, which involves a change in the hybridization of the carbon atom, is relatively slow. A period of a few tenths of a second is typically required for this equilibrium to be established.

<sup>2</sup>The acid dissociation constant  $K_1$  that is commonly quoted for “H<sub>2</sub>CO<sub>3</sub>” is really a *composite* equilibrium constant. The true dissociation constant of H<sub>2</sub>CO<sub>3</sub> is  $K_1' = 10^{-3.5}$ , which makes this acid about a thousand times stronger than is evident from tabulated values of  $K_1$ .

## 2.2 Solution of carbon dioxide in pure water

By combining the preceding equilibria, the following relation between  $C_T$  and the hydrogen ion concentration can be obtained:

$$[\text{H}^+]^4 = [\text{H}^+]^3 K_1 + [\text{H}^+]^2 (C_T K_1 + K_1 K_2 + K_w) - [\text{H}^+] (C_T K_2 + K_w) K_1 - K_1 K_2 K_w = 0 \quad (10)$$

It is almost never necessary to use this exact relation in practical problems. Because the first acid dissociation constant is much greater than either  $K_2$  or  $K_w$ , we can usually treat carbonic acid solutions as if  $\text{H}_2\text{CO}_3$  were monoprotic, so this becomes a standard monoprotic weak acid problem.

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = K_1 = 4.47\text{E-}7 \quad (11)$$

Notice that the charge balance (Eq 9) shows that as the partial pressure of  $\text{CO}_2$  decreases (and thus the concentrations of the other carbonate terms decrease), the pH of the solution will approach that of pure water.

### Problem Example 1

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Calculate the pH of a 0.0250 M solution of  $\text{CO}_2$  in water.

*Solution:* Applying the usual approximation  $[\text{H}^+] = [\text{HCO}_3^-]$  (i.e., neglecting the  $\text{H}^+$  produced by the autoprotolysis of water), the equilibrium expression becomes

$$\frac{[\text{H}^+]^2}{0.0250 - [\text{H}^+]} = 4.47\text{E-}7$$

The large initial concentration of  $\text{H}_2\text{CO}_3$  relative to the value of  $K_1$  justifies the further approximation of dropping the  $[\text{H}^+]$  term in the denominator.

$$\frac{[\text{H}^+]^2}{0.0250} = 4.47\text{E-}7$$

$$[\text{H}^+] = 1.06\text{E-}4; \quad \text{pH} = 3.97$$


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## 2.3 Solution of $\text{NaHCO}_3$ in pure water

The bicarbonate ion  $\text{HCO}_3^-$ , being amphiprotic, can *produce* protons and it can *consume* protons:



The total concentration of protons in the water due to the addition of  $\text{NaHCO}_3$  will be equal to the number produced, minus the number lost; this quantity is expressed by the *proton balance*

$$[\text{H}^+] = [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}_2\text{CO}_3]$$

By making the appropriate substitutions we can rewrite this in terms of  $[\text{H}^+]$ , the bicarbonate ion concentration and the various equilibrium constants:

$$[\text{H}^+] = \frac{K_2[\text{CO}_3^{2-}]}{[\text{H}^+]} + \frac{K_w}{[\text{H}^+]} - \frac{[\text{OH}^-][\text{HCO}_3^-]}{K_1}$$

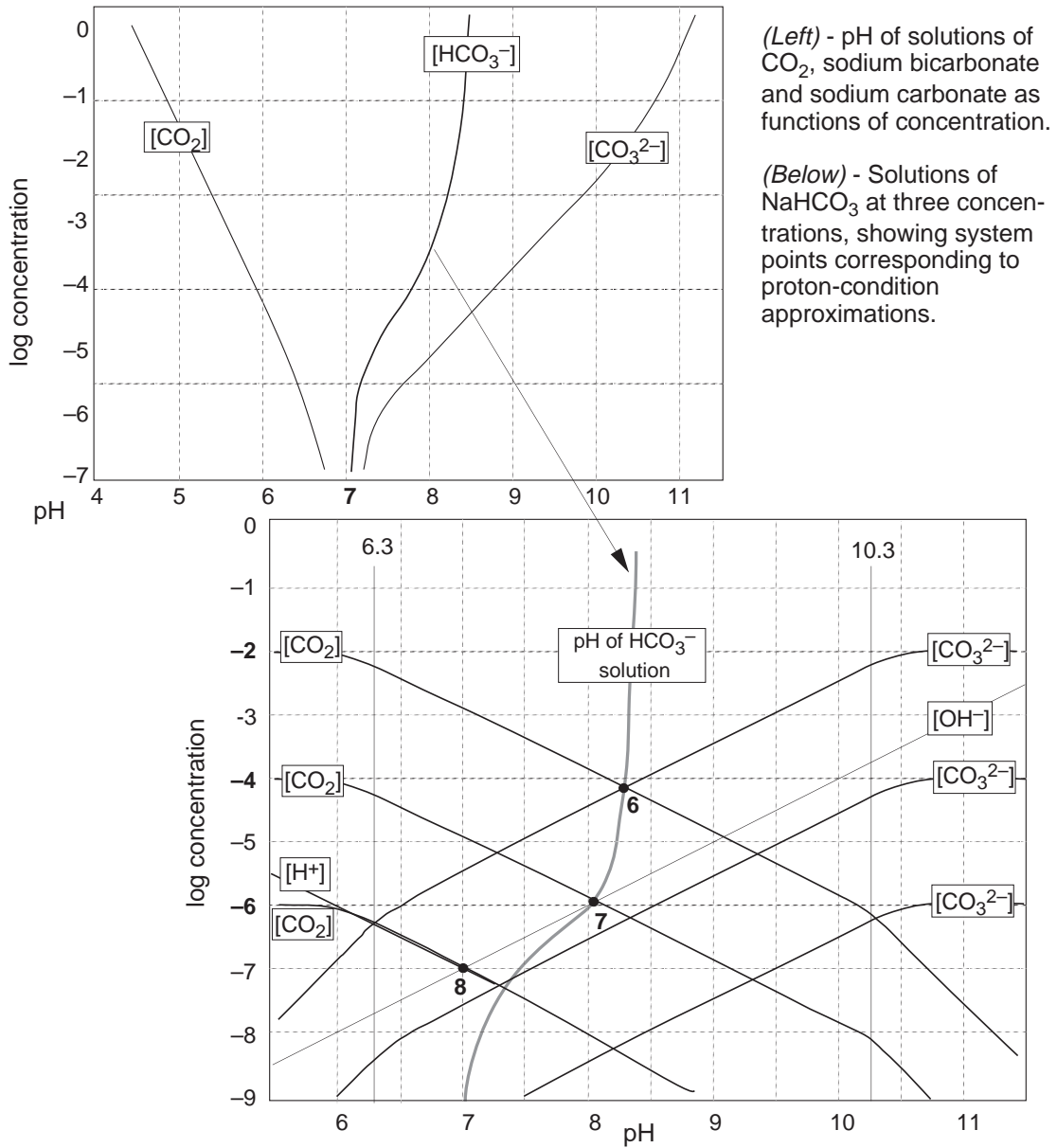


Figure 1: pH of solutions of carbonate species at various dilutions

which we rearrange to

$$[\text{H}^+]^2 = K_2[\text{HCO}_3^-] + K_w - \frac{[\text{H}^+]^2[\text{HCO}_3^-]}{K_1}$$

We solve this for  $[\text{H}^+]$  by collecting terms

$$[\text{H}^+]^2 \left( 1 + \frac{[\text{HCO}_3^-]}{K_1} \right) = K_2[\text{HCO}_3^-] + K_w$$

$$[\text{H}^+] = \sqrt{\frac{K_2[\text{HCO}_3^-] + K_w}{1 + \frac{[\text{HCO}_3^-]}{K_1}}} \quad (12)$$

This expression can be simplified in more concentrated solutions. If  $[\text{HCO}_3^-]$  is greater than  $K_1$ , then the fraction in the denominator may be sufficiently greater than unity that the 1 can be neglected. Similarly, recalling that  $K_2 = 10^{-10.3}$ , it will be apparent that  $K_w$  in the numerator will be small compared to  $K_2[\text{HCO}_3^-]$  when  $[\text{HCO}_3^-]$  is not extremely small. Making these approximations, we obtain the greatly simplified relation

$$[\text{H}^+] = \sqrt{K_1 K_2} \quad (13)$$

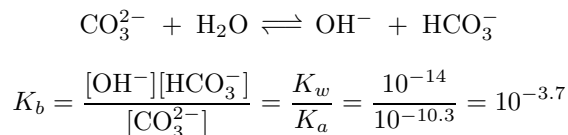
so that the pH is given by

$$\text{pH} = \frac{1}{2}(\text{p}K_1 + \text{p}K_2) = \frac{1}{2}(6.3 + 10.3) = 8.3 \quad (14)$$

Notice that under the conditions at which these approximations are valid, the pH of the solution is independent of the bicarbonate concentration.

## 2.4 Solution of sodium carbonate in pure water

The carbonate ion is the conjugate base of the weak acid  $\text{HCO}_3^-$  ( $K = 10^{-10.7}$ ), so this solution will be alkaline. Except in very dilute solutions, the pH should be sufficiently high to preclude the formation of any significant amount of  $\text{H}_2\text{CO}_3$ , so we can treat this problem as a solution of a monoprotic weak base:



### Problem Example 2

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Calculate the pH of a 0.0012 M solution of  $\text{Na}_2\text{CO}_3$ .

*Solution:* Neglecting the  $\text{OH}^-$  produced by the autoprotolysis of water, we make the usual assumption that  $[\text{OH}^-] = [\text{HCO}_3^-]$ , and thus

$$K_b = \frac{[\text{OH}^-]^2}{0.0012 - [\text{OH}^-]} = 2.00\text{E-}4$$

In this case the approximation  $[\text{OH}^-] \approx \sqrt{K_b C_b}$  is not valid, owing to the magnitude of the equilibrium constant in relation to the carbonate ion concentration. The equilibrium expression must be solved as a quadratic and yields the root  $[\text{OH}^-] = 4.0\text{E-}4$  which corresponds to  $\text{pOH} = 3.4$  or  $\text{pH} = 10.6$ .

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From the preceding example we see that soluble carbonate salts are among the stronger of the weak bases. Sodium carbonate was once known as “washing soda”, reflecting the ability of its alkaline solutions to interact with and solubilize oily substances.

## 3 Distribution of carbonate species in aqueous solutions

In this section we will look closely at the way in which the concentrations of the various carbonate species depend on the pH of the solution. This information is absolutely critical to the understanding of both the chemistry of natural waters and of the physiology of CO<sub>2</sub> exchange between the air and the blood.

The equations that describe these species distributions exactly are unnecessarily complicated, given the usual uncertainties in the values of equilibrium constants in solutions of varying composition. For this reason we will rely mostly on approximations and especially on graphical methods. To construct the graphs we need to look again at solutions of each of the substances carbon dioxide, sodium bicarbonate, and sodium carbonate in pure water. This time, however, we can get by with much simpler approximations because the logarithmic graphs are insensitive to small numerical errors.

### 3.1 Open and closed systems

First, however, we must mention a point that complicates matters somewhat. If a carbonate-containing solution is made alkaline, then the equilibrium



will be shifted to the right. Thus whereas  $C_T = [\text{H}_2\text{CO}_3^*] = 10^{-5}$  when pure water comes to equilibrium with the atmosphere, the total carbonate ( $C_T$ , Eq 8) will exceed that of  $\text{H}_2\text{CO}_3^*$  if the pH of the solution is high enough to promote the formation of bicarbonate and carbonate ions. In other words, alkaline carbonate solutions will continue to absorb carbon dioxide until the solubility limits of the cation salts are reached. You may recall that the formation of a white precipitate of  $\text{CaCO}_3$  in limewater (a saturated solution of  $\text{CaCO}_3$ ) is a standard test for  $\text{CO}_2$ .

Thus before we can consider how the concentrations of the different carbonate species vary with the pH, we must decide whether the solution is likely to be in equilibrium with the atmosphere. If it is, then  $C_T$  will vary with the pH and we have what is known as an *open* system. Alternatively, if  $C_T$  remains essentially constant, the system is said to be *closed*. Whether we consider a particular system to be open or closed is a matter of judgement based largely on kinetics: the transport of molecules between the gas phase and the liquid phase tends to be a relatively slow process, so for many practical situations (such as a titration carried out rapidly) we can assume that no significant amount of  $\text{CO}_2$  can enter or leave the solution.

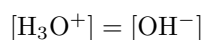
- An *open* system is one in which  $P_{\text{CO}_2}$  is constant; this is the case for water in an open container, for streams and shallow lakes, and for the upper, wind-mixed regions of the oceans.
- In a *closed* system, transport of  $\text{CO}_2$  between the atmosphere and the system is slow or nonexistent, so  $P_{\text{CO}_2}$  will change as the distribution of the various carbonate species is altered. Titration of a carbonate solution with strong base, if carried out rapidly, approximates a closed system, at least until the pH becomes very high. The deep regions of stratified bodies of water and the air component of soils are other examples of closed systems.
- Each of these carbonate systems can be further classified as *homogeneous* or *heterogeneous*, depending on whether equilibria involving solid carbonates need be considered. Thus the bottom part of a stratified lake whose floor is covered with limestone sediments is a closed, heterogeneous system, as is a water treatment facility in which soda ash, acid or base, and  $\text{CO}_2$  are added (and in which some  $\text{CaCO}_3$  precipitates). An example of an open, heterogeneous system would be the forced reareation basin of an activated sludge plant, in which equilibrium with  $\text{CaCO}_3$  cannot be established owing to the short residence times.



## 3.2 Closed systems

The log  $C$ -pH diagram for a closed system is basically the same as for any diprotic acid. The two  $pK_a$ s along with  $C_T$  locate the distribution curves for the various carbonate species. We will now consider solutions initially consisting of  $10^{-5} M$   $CO_2$  (that is, in equilibrium with the atmosphere) which have been isolated from the atmosphere and then titrated to their successive equivalence points.

**Proton balance** In this, and in the section that follows on open systems, we will make use of an equilibrium condition known as *proton balance*. This is essentially a mass balance on protons; it is based on the premise that protons, or the hydrogen atoms they relate to, are conserved. A trivially simple example of a proton balance is that for pure water:



This says that every time a hydronium ion is produced in pure  $H_2O$ , a hydroxide ion will also be formed. Notice that  $H_2O$  itself does not appear in the equation; proton-containing species initially present in the system define what is sometimes called the *proton reference level* and should never appear in a proton balance. The idea is that these substances react to produce proton-occupied states and proton-empty states in equal numbers. Thus on one side of the proton balance we put all species containing more protons than the reference species, while those containing fewer protons are shown on the other side.

### Solution of carbon dioxide in pure water

The proton reference substances for this solution are  $H_2O$  and  $H_2CO_3$ , the proton balance expression is

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \quad (15)$$

The factor of 2 is required for  $[CO_3^{2-}]$  because this substance would consume two moles of  $H^+$  to be restored to the  $H_2CO_3$  reference level. Because the solution will be acidic, we can neglect all but the bicarbonate term on the right side, thus obtaining the approximation

$$[H^+] = [HCO_3^-] + \dots \quad (16)$$

which corresponds to point **1** in Fig. 2a.

**Solution of  $NaHCO_3$  in pure water** The proton balance is

$$[H^+] + [H_2CO_3^*] = [CO_3^{2-}] + [OH^-] \quad (17)$$

At all except the lowest concentrations the solution will be well buffered (see Fig. 1) and the major effect of changing  $[A^-]$  will be to alter the extent of autoprotolysis of  $HCO_3^-$ . The solution will be sufficiently close to neutrality that we can drop the  $[H^+]$  and  $[OH^-]$  terms:

$$[H_2CO_3^*] \approx [CO_3^{2-}] \quad (\text{high concentrations}) \quad (18)$$

This corresponds to point **2** in Fig. 2a, and to points **6** and **7** in Fig. 1.

**Solution of  $Na_2CO_3$**  The proton balance for a carbonate solution is

$$[H^+] + 2[H_2CO_3^*] + [HCO_3^-] = [OH^-] \quad (19)$$

and the appropriate simplifications will depend on the concentration of the solution. At high concentrations ( $C_T > 10^{-3} M$ ) we can write

$$[\text{H}_2\text{CO}_3] \approx \frac{1}{2}[\text{OH}^-] \quad (\text{high concentrations}) \quad (20)$$

In the range ( $10^{-4} M > C_T > 10^{-7} M$ ) the lower pH will reduce the importance of  $\text{CO}_3^{2-}$  and we have

$$[\text{HCO}_3^-] \approx [\text{OH}^-] \quad (\text{low concentrations}) \quad (21)$$

This condition occurs at point **3** in Fig. 2a.

A third case would be the trivial one of an extremely dilute solution of  $\text{NaHCO}_3$  in which we have essentially pure water and  $[\text{H}^+] \approx [\text{OH}^-]$ .

### 3.3 Open systems

If the system can equilibrate with the atmosphere, then

$$-\log[\text{H}_2\text{CO}_3^*] = 5 \quad (22)$$

and  $[\text{H}_2\text{CO}_3^*]$  plots as a horizontal line in Fig. 2b. Substituting this constant  $\text{H}_2\text{CO}_3^*$  concentration into the expression for  $K_1$ , we have

$$[\text{HCO}_3^-] = \frac{10^{-5}K_1}{[\text{H}^+]}$$

so that

$$-\log[\text{HCO}_3^-] = 5 - \text{pH} + \text{p}K_1 = 11.3 - \text{pH} \quad (23)$$

Similarly, for  $\text{CO}_3^{2-}$  we can write

$$[\text{CO}_3^{2-}] = \frac{10^{-5}K_1K_2}{[\text{H}^+]^2}$$

$$-\log[\text{CO}_3^{2-}] = 5 + \text{p}K_1 + \text{p}K_2 - 2\text{pH} = 21.6 - 2\text{pH} \quad (24)$$

These relations permit us to plot the log- $C$  diagram of Fig. 2b. Because the condition

$$C_{\text{total carbonate}} = \text{constant}$$

no longer applies, increasing the concentration of one species does not subtract from that of another, so all the lines are straight. Point **4** corresponds to the same proton condition for a solution of  $\text{CO}_2$  as in the closed system. For  $10^{-5} M$  solutions of sodium bicarbonate and sodium carbonate, it is necessary to write a charge balance that includes the metal cation. Thus for  $\text{NaHCO}_3$  we have

$$[\text{H}^+] + [\text{Na}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$$

or

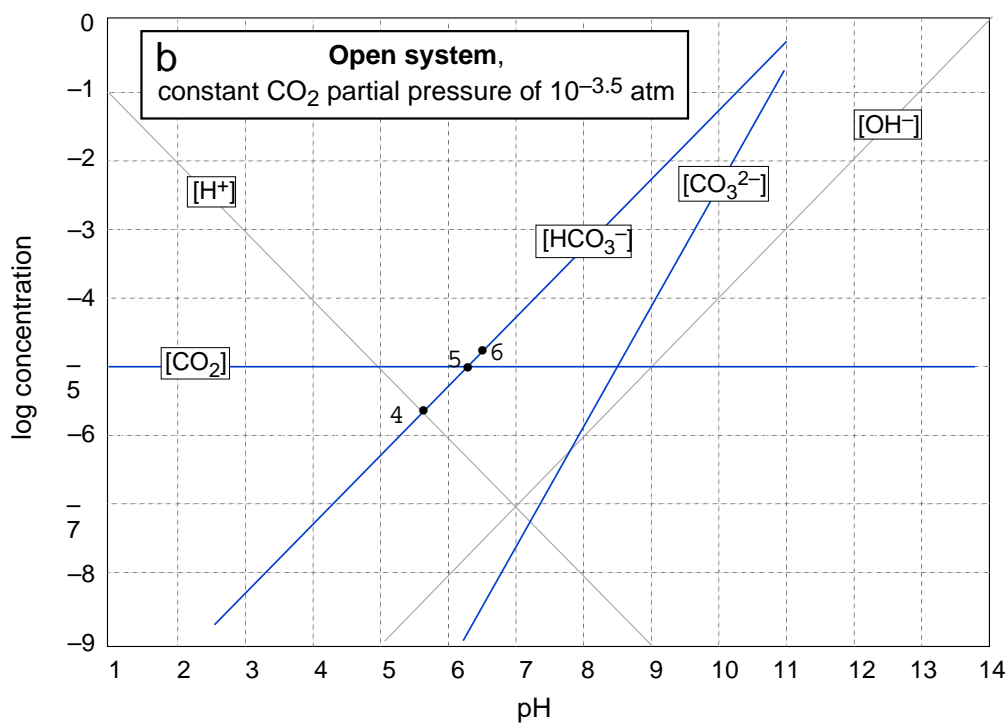
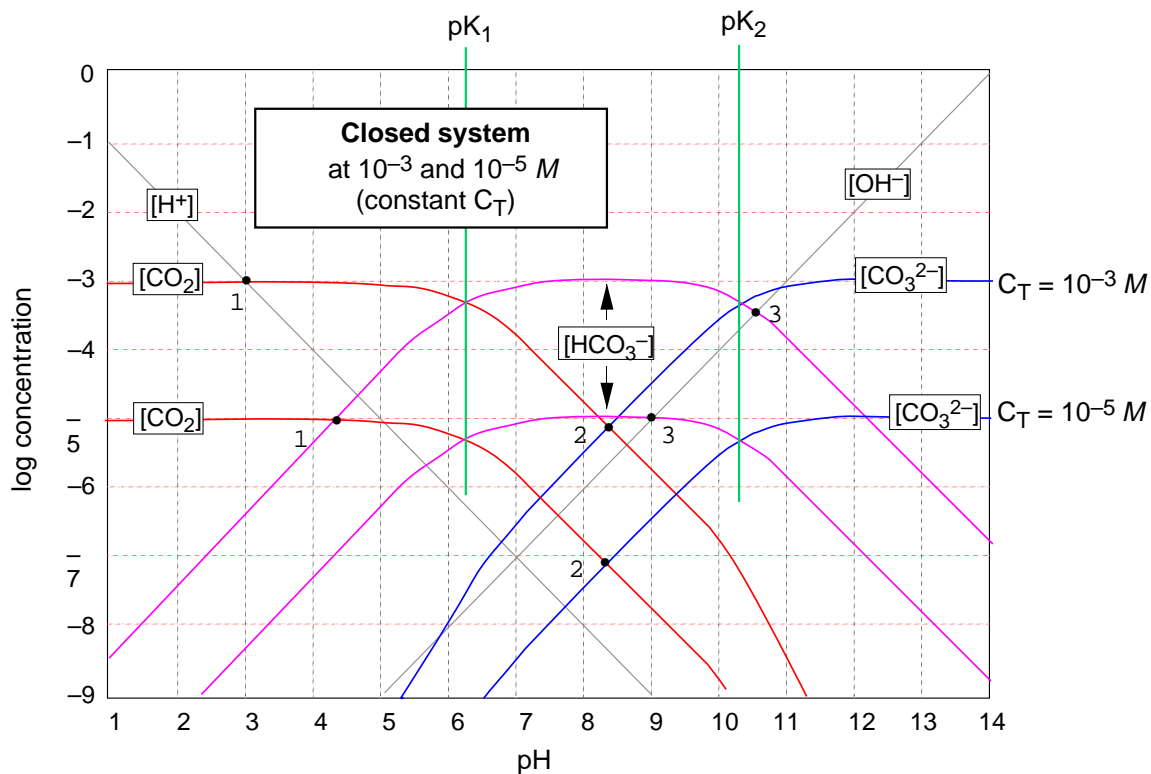
$$[\text{Na}^+] \approx [\text{HCO}_3^-] = 10^{-5} M \quad (\text{point } \mathbf{5}) \quad (25)$$

Similarly, for a  $10^{-5} M$  solution of  $\text{Na}_2\text{CO}_3$ ,

$$[\text{H}^+] + [\text{Na}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$$

and, given the rather low concentrations, we can eliminate all except the two terms adjacent to the equality sign:

$$[\text{Na}^+] \approx [\text{HCO}_3^-] = 2 \times 10^{-5} M \quad (\text{point } \mathbf{6}) \quad (26)$$



CO-02

Figure 2: log  $C$ -pH diagrams for open and closed carbonate systems.

solution	$C_{T,CO_2}$		pH	
	closed	open	closed	open
H <sub>2</sub> CO <sub>3</sub>	10 <sup>-5.0</sup>	10 <sup>-4.9</sup>	5.7	5.7
NaHCO <sub>3</sub>	10 <sup>-5.0</sup>	10 <sup>-4.7</sup>	7.6	6.3
Na <sub>2</sub> CO <sub>3</sub>	10 <sup>-5.0</sup>	10 <sup>-4.5</sup>	9.0	6.6

Table 4: Comparison of open and closed carbonate solutions.

To examine the way the pH of a solution of carbon dioxide depends on the partial pressure of this gas we can combine the Henry's law expression Eq 2 with the proton balance

$$[H^+] \approx [HCO_3^-]$$

to give

$$[H^+]^2 \approx K_1 K_H P_{CO_2} \quad (27)$$

Using the conventional value of  $K_H = 10^{-1.5}$  this becomes

$$pH \approx 3.9 - \frac{1}{2} \log P_{CO_2} \quad (28)$$

Notice that a 100-fold increase in  $P_{CO_2}$  will raise the hydrogen ion concentration by only a factor of ten. This shows that a body of CO<sub>2</sub>-saturated water can act as a buffer even in the absence of dissolved carbonate salts.

### 3.4 Comparison of open and closed carbonate systems

The most striking difference between the log  $C$ -pH diagrams for closed and open systems is that in the latter, the concentrations of bicarbonate and carbonate ions increase without limit (other than that imposed by solubility) as the pH is raised. This reflects, of course, the essentially infinite supply of CO<sub>2</sub> available if the atmosphere is considered part of the system.

A close look at the exact values of pH and total carbonate for 10<sup>-5</sup> M solutions of H<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> shows that in the latter two solutions, the pH will be higher if the system is closed, even though the total carbonate concentration is higher than in the open system. One consequence of this effect is that the pH of groundwater will fall as it emerges from a path through subsurface cracks and fissures (a closed system) and come into contact with the atmosphere at a spring; the reduced pH brings about erosion and dissolution of surrounding limestone deposits, sometimes leading to the formation of extensive caves.

The other point of general environmental significance is that the pH of a sample of pure water exposed to the atmosphere will fall to 5.7. As long as the water does not acquire any alkalinity (i.e., Na<sup>+</sup>, Ca<sup>2+</sup>, etc.), the pH will be independent of whether the system remains open or closed. Note that in this sense, *all* rain is expected to be somewhat acidic.

## 4 Alkalinity and acidity of carbonate-containing waters

The concepts of alkalinity (acid-neutralizing capacity) and acidity (base neutralizing capacity) are extremely important in characterizing the chemical state of natural waters, which always contain carbon dioxide and carbonates. Silicates, borates, phosphates, ammonia, and organic acids and bases are also frequently present. In most natural waters the concentrations of these other species are usually sufficiently

low that they can be neglected, but in special cases (outflow of waste treatment plants, for example) they must be taken into account.

Considering a solution containing carbonates only, it can be characterized at any pH as consisting of a mixture of  $\text{CO}_2$  at a concentration of  $C_T$  together with some arbitrary amount of a strong base such as NaOH. The charge balance for such a solution is

$$[\text{H}^+] + [\text{Na}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (29)$$

The alkalinity, defined as the amount of strong acid required to titrate the solution back to one of pure  $\text{H}_2\text{CO}_3^*$ , is just the amount of NaOH we used to prepare the solution in the first place; thus  $[\text{Alk}] = [\text{Na}^+]$  and the alkalinity is given by

$$[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (30)$$

The alkalinity and acidity of a solution is always defined with respect to some arbitrary *proton reference level*, or pH; this is the pH at the endpoint of a neutralization carried out by adding strong acid or strong base to the solution in question. For waters containing a diprotic system such as carbonate, three different reference pH values are defined, and thus there are several acidity- and alkalinity scales. These pH's correspond roughly to the closed-system values in Table 4, except that in most natural waters the equivalent  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  concentrations will be higher owing to dissolution of sediments.

The indicators methyl orange ( $\text{p}K_a = 4.5$ ) and phenolphthalein ( $\text{p}K_a = 8.3$ ) have traditionally been used to detect the endpoints corresponding to solutions of pure  $\text{H}_2\text{CO}_3$  and pure  $\text{NaHCO}_3$ , respectively. The pH values 4.5 and 8.3 are therefore referred to as the methyl orange and phenolphthalein endpoints, and these serve as operational definitions of two of the three reference points of the acidity-alkalinity scale for the carbonate system. The third endpoint, corresponding to a solution of  $\text{Na}_2\text{CO}_3$  in pure water, occurs at too high a pH (usually between 10-11) to be reliably detectable by conventional open-air titration.

All natural waters that have had an opportunity to acquire electrolytes contain some alkalinity, and can be titrated to the phenolphthalein or methyl orange endpoints by adding strong acid. The following definitions are widely used and are important for you to know; refer to Fig. 4 while studying them, and see Table 5 for a summary.

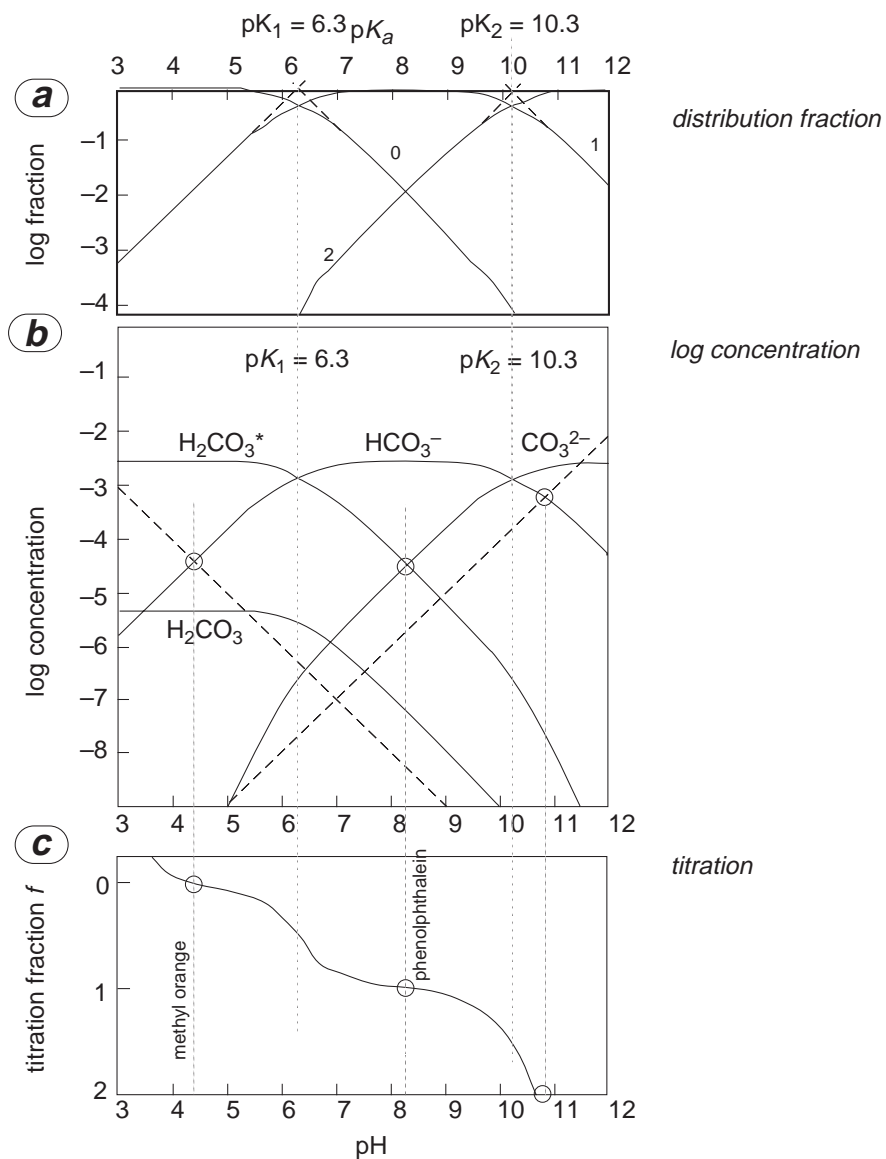
**Total alkalinity** is the number of equivalents per litre of strong acid required to titrate the solution to a pH of 4.5. In doing so, all carbonate species become totally protonated. The volume of acid required to attain this endpoint is referred to as  $V_{\text{mo}}$ .

**Carbonate alkalinity** refers to the quantity of strong acid required to titrate the solution to the phenolphthalein endpoint. At this point, all  $\text{CO}_3^{2-}$  has been converted to  $\text{HCO}_3^-$ . If the pH of the solution was at or below 8.3 to begin with, the carbonate alkalinity is zero or negative.

**Total acidity** is the number of moles/litre of  $\text{OH}^-$  that must be added to raise the pH of the solution to 10.8, or to whatever pH is considered to represent a solution of pure  $\text{Na}_2\text{CO}_3$  in water at the concentration of interest.

**$\text{CO}_2$  acidity** is the amount of  $\text{OH}^-$  required to titrate a solution to a pH of 8.3. This assumes, of course, that the pH of the solution is initially below 8.3. Such a solution contains  $\text{H}_2\text{CO}_3$  as a major component, and the titration consists in converting the  $\text{H}_2\text{CO}_3$  into  $\text{HCO}_3^-$ .

**Caustic alkalinity** is the number of equivalents per litre of strong acid required to reduce the pH of an alkaline solution to 10.8. A solution possessing caustic alkalinity must contain significant quantities of a base stronger than  $\text{CO}_3^{2-}$ .



[Stumm & Morgan: Aquatic Chemistry]

These diagrams, adapted from Stumm & Morgan, are for a closed natural water system with  $C_T = 10^{-2.5}$  M and an ionic strength of about  $10^{-2}$  M. All are shown with the same pH scale. **a:** Ionization fractions as a function of pH. **b:** Logarithmic concentration diagram, showing curves for both  $H_2CO_3^*$  (total aqueous  $CO_2$ ) and for the actual  $H_2CO_3$  species, which is seen to be a considerably stronger acid. **c:** Alkalimetric or acidimetric titration curve. The circles in **b** and **c** denote the equivalence points corresponding to pure  $C_T$ -molar solutions of  $H_2CO_3^*$ ,  $NaHCO_3$ , and  $Na_2CO_3$ ; notice that there is no pH jump at the latter equivalence point, owing to the buffering action of  $OH^-$  at this high pH.

Figure 3: Titration curve and pH-pC diagram for the carbonate system.

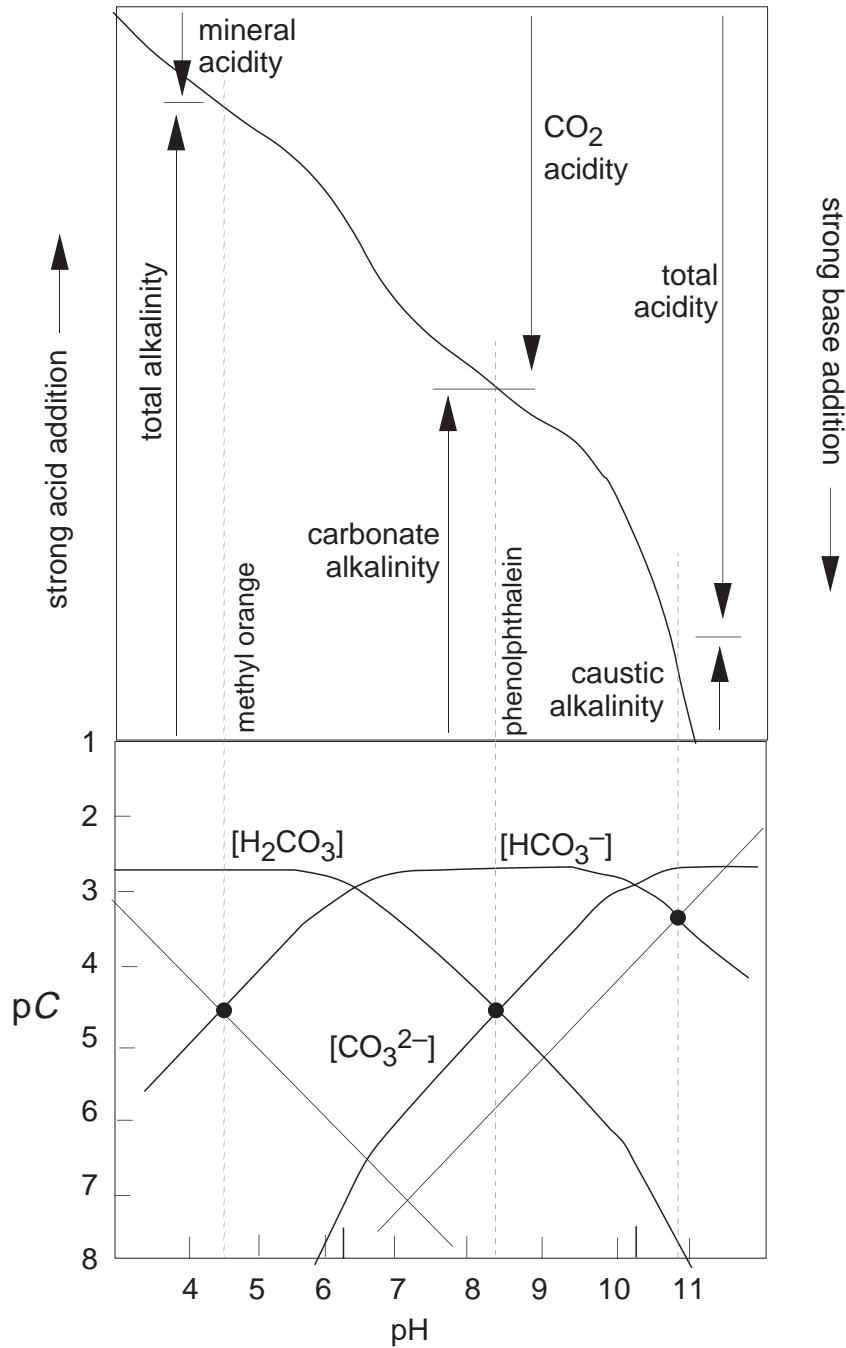


Figure 4: Titration and distribution curves illustrating alkalinity and acidity

<i>equivalence point</i>	<i>proton condition</i>	<i>definition</i>
$\text{pH}_{\text{H}_2\text{CO}_3^*} = 4.5$	$[\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$	total acidity = $[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] = [\text{H}^+]$ mineral acidity = $[\text{H}^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-]$
$\text{pH}_{\text{HCO}_3^-} = 8.3$	$[\text{H}^+] + [\text{H}_2\text{CO}_3^*] = [\text{CO}_3^{2-}] + [\text{OH}^-]$	carbonate alkalinity = $[\text{CO}_3^{2-}] - [\text{OH}^-] - [\text{H}_2\text{CO}_3^*] - [\text{H}^+]$ CO <sub>2</sub> acidity = $[\text{H}^+] + [\text{H}_2\text{CO}_3^*] - [\text{CO}_3^{2-}] - [\text{OH}^-]$
$\text{pH}_{\text{CO}_3^{2-}} \simeq 10.8$	$[\text{H}^+] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-*}] = [\text{OH}^-]$	caustic alkalinity = $[\text{OH}^-] - [\text{HCO}_3^-] - 2[\text{H}_2\text{CO}_3^*] - [\text{H}^+]$ total acidity = $[\text{H}^+] + [\text{HCO}_3^-] + 2[\text{H}_2\text{CO}_3^*] = [\text{OH}^-]$

Table 5: Definitions of alkalinity and acidity in carbonate solutions.

**Mineral acidity** is the amount of OH<sup>-</sup> required to raise the pH of an acidic solution to 4.5. Such a solution must contain a stronger acid than H<sub>2</sub>CO<sub>3</sub>, usually a “mineral” acid such as H<sub>2</sub>SO<sub>4</sub> or HNO<sub>3</sub>. Acid mine drainage and acid rain commonly possess mineral acidity.

### Problem Example 3

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A 100-mL sample of a natural water whose pH is 6.6 requires 12.2 mL of 0.10M HCl for titration to the methyl orange end point and 5.85 mL of 0.10M NaOH for titration to the phenolphthalein end point. Assuming that only carbonate species are present in significant quantities, find the total alkalinity, carbon dioxide acidity and the total acidity of the water.

*Solution:* First, note that since the pH is below 8.3, bicarbonate is the major alkalinity species.

*Total alkalinity* (conversion of all carbonates to CO<sub>2</sub>): 12.2 mM/L.

*CO<sub>2</sub> acidity* (conversion of CO<sub>2</sub> to HCO<sub>3</sub><sup>-</sup>): 5.85 mM/L

*total acidity* (conversion of all carbonate species to CO<sub>3</sub><sup>2-</sup>): because it is impractical to carry out this titration, we make use of the data already available. Conversion of the initial CO<sub>2</sub> to HCO<sub>3</sub><sup>-</sup> would require 5.85 mM/L of NaOH, and then an additional equal amount to go HCO<sub>3</sub><sup>-</sup>. Similarly, the 12.2 mM/L of HCO<sub>3</sub><sup>-</sup> initially present will require this same quantity of NaOH for conversion to CO<sub>3</sub><sup>2-</sup>. The total acidity is thus  $(5.85 + 5.85 + 12.2) = \underline{23.8 \text{ mM/L}}$ .

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Alkalinity and acidity are normally determined (and in a sense are *defined*) by standardized analytical techniques which attempt to minimize the effects of contamination of the solutions by atmospheric CO<sub>2</sub>. The values, often represented by [Alk] and [Acy], are expressed in moles or equivalents per litre. Another very common convention is to express total alkalinity in terms of milligrams per litre of CaCO<sub>3</sub>. This simply refers to the amount of strong acid required to react completely with the specified mass of this compound. Since the molar mass of CaCO<sub>3</sub> is 100.08 g/mol, the conversion is a simple one; for example, a total alkalinity of 500 mg/l as CaCO<sub>3</sub> is equivalent to [Alk] = 10meq/L.

From Fig. 3 it is apparent that [Alk], pH, and pC (total carbonate) are related in pure carbonate solutions; if any two of these are measured, the third can be calculated. Instead of using direct calculations (which can be developed from the analytical definitions in Table 7), a graphical method is commonly employed. The graph in Fig. 5 shows how [Alk] varies with C<sub>T,CO<sub>3</sub></sub> at various values of pH. Addition of strong acid or base corresponds to movement along the vertical axis (i.e., C<sub>T,CO<sub>3</sub></sub> remains constant in a closed system). Addition or removal of CO<sub>2</sub> corresponds to horizontal movement, since changes in



<i>Volume condition</i>	<i>Predominant form of alkalinity</i>	<i>approximate concentration</i>
$V_p = V_{mo}$	$\text{CO}_3^{2-}$	$[\text{CO}_3^{2-}] = V_p \times N/V$
$V_p = 0$	$\text{HCO}_3^-$	$[\text{HCO}_3^-] = V_{mo} \times N/V$
$V_{mo} = 0$	$\text{OH}^-$	$[\text{OH}^-] = V_p \times N/V$
$V_{mo} > V_p$	$\text{CO}_3^{2-}$ and $\text{HCO}_3^-$	$[\text{CO}_3^{2-}] = V_p \times N/V$ $[\text{HCO}_3^-] = (V_{mo} - V_p) \times N/V$
$V_p > V_{mo}$	$\text{OH}^-$ and $\text{CO}_3^{2-}$	$[\text{CO}_3^{2-}] = V_{mo} \times N/V$ $[\text{OH}^-] = (V_p - V_{mo}) \times N/V$

$V_{mo}$  and  $V_p$  are the volumes of strong acid of normality  $N$  required to reach the end points at pH 4.5 and 8.3, respectively.  $V$  is the initial volume of the solution.

Table 6: Approximate relations between the results of an alkalinity titration and the concentrations of predominant species in carbonate solutions.

<i>quantity</i>	<i>expression</i>
(1) total alkalinity [Alk]	$C_{T,\text{CO}_3}(\alpha_1 + 2\alpha_2) + K_w/[\text{H}^+] - [\text{H}^+]$
(2) carbonate alkalinity	$C_{T,\text{CO}_3}(\alpha_2 - \alpha_0) + K_w/[\text{H}^+] - [\text{H}^+]$
(3) caustic alkalinity	$K_w/[\text{H}^+] - [\text{H}^+] - C_{T,\text{CO}_3}(\alpha_1 - \alpha_0)$
(4) total acidity	$C_{T,\text{CO}_3}(\alpha_1 + 2\alpha_0) + [\text{H}^+] - K_w/[\text{H}^+]$
(5) $\text{CO}_2$ acidity	$C_{T,\text{CO}_3}(\alpha_0 - \alpha_2) + [\text{H}^+] - K_w/[\text{H}^+]$
(6) mineral acidity	$[\text{H}^+] - K_w/[\text{H}^+] - C_{T,\text{CO}_3}(\alpha_1 + 2\alpha_2)$

Table 7: Analytical definitions of alkalinity and acidity for carbonate solutions.

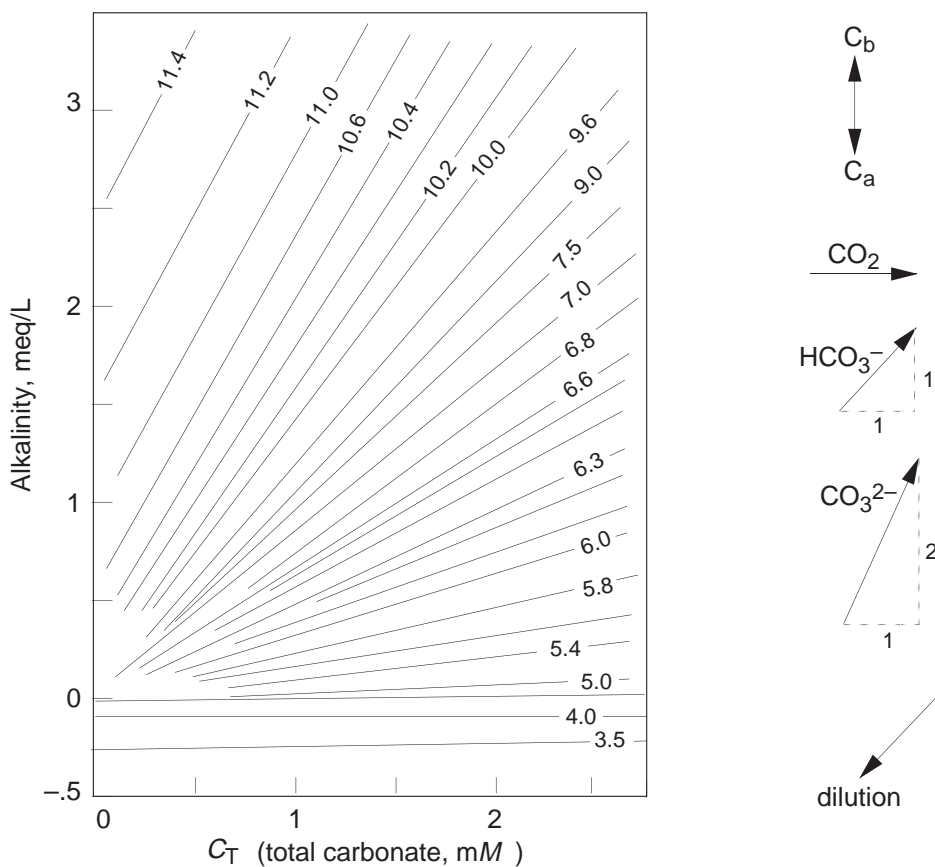


Figure 5: Deffeyes diagram relating the pH, alkalinity, and  $C_{T,CO_3}$ .

$[\text{H}_2\text{CO}_3^*]$  have no effect on the alkalinity. Addition or removal of bicarbonate and carbonate is represented by movement at angles of  $45^\circ$  and  $60^\circ$ , respectively, reflecting the 1:1 and 2:1 ratios between the amounts of acid required to titrate these two species to the methyl orange endpoint.

These considerations are quite important for understanding the behavior of natural waters in which carbonate species are the principal buffering agents. In particular:

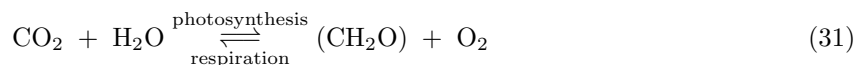
- Alkalinity and acidity are conservative parameters, unaffected by temperature, pressure, and activity coefficients. Note that this is *not* true for the pH, which will vary with all of these factors.
- A water can simultaneously possess both alkalinity and acidity. Indeed, this is the usual case over the pH range in which  $\text{HCO}_3^-$  predominates.
- Addition or removal of  $\text{CO}_2$  (e.g., by the action of organisms) will have no effect on [Alk]. However this will affect both the acidity and  $C_{\text{T,CO}_3}$ ; an increase in  $[\text{H}_2\text{CO}_3^*]$  will raise both of these quantities.
- The activities of photosynthetic and respiratory organisms commonly involve the addition or removal of ions such as  $\text{H}_3\text{O}^+$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{HPO}_4^{2-}$ , etc. Charge conservation requires that the uptake of an ion such as  $\text{NH}_4^+$  must be accompanied by the uptake of  $\text{H}^+$  or the release of  $\text{OH}^-$ , either of which will increase the alkalinity. Processes of this kind take place on a large scale in both aquatic and non-aquatic ecosystems. The flow of groundwater and runoff from the land can affect the pH and alkalinity of adjacent bodies of water, especially in areas of intense agricultural activity.
- Addition or removal of solid  $\text{CaCO}_3$  or other carbonates will have no effect on the acidity. Thus acidity is conserved in solutions which are brought into contact with calcite and similar sediments.
- In a system that is closed to the atmosphere and is not in contact with solid carbonates, the total carbonate concentration  $C_{\text{T,CO}_3}$  is unchanged by the addition of strong acid or strong base.
- The presence of mineral acidity or caustic alkalinity in a natural water is indicative of a source of industrial pollution. The limits of pH represented by these two conditions correspond roughly to those that are tolerated by most living organisms.

## 5 Effects of biological processes on pH and alkalinity

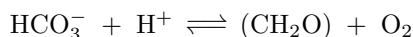
Most natural waters contain organisms whose activities affect, and in many cases may exert a major control over, the pH and alkalinity.

### 5.1 Photosynthesis

Photosynthesis and respiration by algae correspond to opposite directions of the reaction

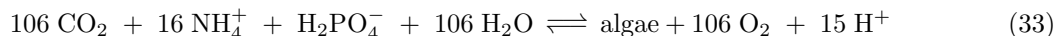
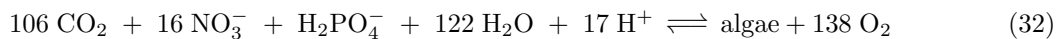


Addition or removal of  $\text{CO}_2$  have no direct effect on the alkalinity, but these processes do affect the pH and are responsible for the significant diurnal changes in pH that can be observed in ponds and small lakes. In more acidic waters this change is minimal, but above 6.3 where bicarbonate becomes the major species the above reaction becomes



Plant growth also requires the uptake of nitrogen and phosphorus which affect both the pH and the alkalinity. From the observed average ratios of the major elemental constituents of algal biomass we can

use  $C_{106}H_{263}O_{110}N_{16}P$  as the “formula” for algae. Depending on whether the nitrogen is taken up as nitrate or ammonium ion, we can write the following two more complete stoichiometric descriptions of photosynthesis:



These processes which involve the assimilation of cations and anions such as  $\text{NH}_4^+$  and  $\text{NO}_3^-$  affect the alkalinity as a result of the uptake or release of  $\text{H}^+$  (or  $\text{OH}^-$ ) that is required to maintain charge balance. From the stoichiometry of these equations we can see that

- When the major nitrogen source is  $\text{NH}_4^+$ , the alkalinity decreases by  $\frac{15}{106} = 0.14$  mol per mole of carbon fixed.
- When the major nitrogen source is  $\text{NO}_3^-$ , the alkalinity increases by  $\frac{17}{106} = 0.16$  mol per mole of carbon fixed.

The pH changes brought about by assimilation or release of phosphate and nitrogen are usually quite small compared to those due to  $\text{CO}_2$  exchange.

#### Problem Example 4

Estimate the change in the pH that would accompany the aerobic decomposition of organic matter in a lake water having an initial pH of 6.90, an alkalinity of 0.00012 mol/L and containing 6  $\mu\text{g}$  of carbon per mL. Assume that  $\text{NH}_4^+$  is the principal form of nitrogen released.

*Solution:* Both  $C_T$  and the alkalinity change here; it is easiest to find how each changes the pH separately. We begin by calculating the pH change due to the increase in  $\text{CO}_2$  at constant alkalinity, using Eq 30 (eq (1) in Table 7)

$$[\text{Alk}] = C_{T,\text{CO}_3}(\alpha_1 + 2\alpha_2) + [\text{OH}^-] - [\text{H}^+] \quad (30)$$

Under the initial conditions  $C_T = 1.61$  mM and  $\alpha_2$  is negligible. Addition of the  $\text{CO}_2$  raises  $C_T$  to 2.11 mM and reduces the pH to about 6.5.

Next, we calculate the change in the pH that would accompany the alkalinity decrease (due to the uptake of  $\text{H}^+$ ) at constant  $C_T$ . This is just  $\frac{15}{106} \times .00050$ . This new alkalinity is substituted into the Eq 30 along with the value of  $\alpha_1$  for pH 6.5.

process	reaction	change in pH	$\Delta$ [Alk]
sulfate reduction	$\text{SO}_4^{2-} + 2 (\text{CH}_2\text{O}) + 2 \text{H}^+ \longrightarrow \text{H}_2\text{S} + 2 \text{H}_2\text{O} + 2 \text{CO}_2$	increases above 6.3, decreases below 6.3	+2 eq
nitrogen fixation (accompanying photosynthesis)	$106 \text{CO}_2 + 8 \text{N}_2 + \text{H}_2\text{PO}_4^- + \text{H}^+ \longrightarrow \text{algae} + 118 \text{O}_2$	increases	+0.13 eq per mole of $\text{N}_2$ fixed
nitrification	$\text{NH}_4^+ + \frac{3}{2} \text{O}_2 \longrightarrow \text{NO}_2^- + 2\text{H}^+ + \text{H}_2\text{O}$ $\text{NO}_2^- + \frac{1}{2} \text{O}_2 \longrightarrow \text{NO}_3^-$	decreases no change	2 eq per mole no change
denitrification	$4 \text{NO}_3^- + 5 (\text{CH}_2\text{O}) + 4 \text{H}^+ \longrightarrow 2 \text{N}_2 + 5 \text{CO}_2 + 7 \text{H}_2\text{O}$	increases below 6.3	+1 eq per mole
methane formation	$(\text{CH}_2\text{O}) + (\text{CH}_2\text{O}) \longrightarrow \text{CH}_4 + \text{CO}_2$	decreases below 6.3	no change

Table 8: Microbial processes and their effects on alkalinity and pH

## 5.2 Other microbial processes

A number of other processes which also involve oxidation or reduction are mediated by organisms that occur in soils. Transfer of soil water and agricultural drainage into adjacent bodies of water can have significant effects on these aquatic ecosystems. The major reactions and their effects on the pH and alkalinity are summarized in Table 8.

component	seawater	river water
Na <sup>+</sup>	468.04	0.274
K <sup>+</sup>	10.00	0.059
Mg <sup>2+</sup>	53.27	0.169
Ca <sup>2+</sup>	10.33	0.375
Sr <sup>2+</sup>	0.10	
Cl <sup>-</sup>	545.88	0.220
SO <sub>4</sub> <sup>2-</sup>	28.20	0.117
Br <sup>-</sup>	0.83	
F <sup>-</sup>	0.07	0.0053
carbonate	2.2 - 2.5	0.957
borate	0.43	
silicate	0.001 - 0.1	0.218
phosphate	0.0001 - 0.005	
NO <sub>3</sub> <sup>-</sup>	0.0001 - 0.05	0.017
pH	(7.4 to 8.3)	(6.0 to 8.5)
alkalinity	2.3 - 2.6	
ionic strength	700	2.09

The concentrations are expressed in millimoles per kg and refer to normal seawater and world average river water.

Table 9: Composition of seawater and river water

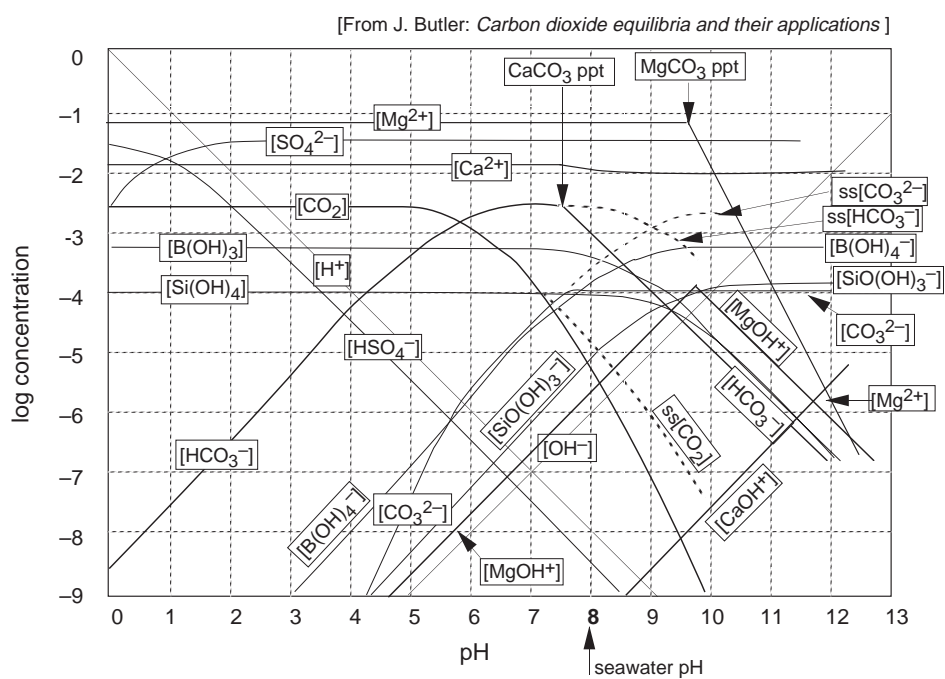
## 6 Seawater

The chemistry of the oceans is a huge subject that we cannot begin to do justice to here. As can be seen in Table 9, seawater is composed mostly of a few major cations and anions that account for the bulk of its dissolved solids content. The latter is called the *salinity* which is usually expressed as parts per thousand by weight. Although the salinity of seawater can vary locally (it is lower in estuaries and higher in regions of ice formation and in semi-enclosed temperate oceans such as the mediterranean), the relative amounts of the major ions remain remarkably constant. Although these ions are not directly involved in the equilibria we are considering here, the relatively high ionic strength of seawater does affect the equilibrium constants and must be taken into account in accurate calculations. Activity coefficients are around 0.7 for univalent ions and 0.3 for divalent ions.

### 6.1 Effects of oceanic circulation

Although the the major ionic components of seawater retain a nearly constant concentration ratio throughout the oceans, this is not the case for some of the minor ones that are involved in biological processes. During daylight hours, phytoplankton photosynthesis can considerably reduce total dissolved carbon ([TDC]) and remove phosphate completely from surface waters. Those phytoplankton and zooplankton that produce calcite skeletal material remove CaCO<sub>3</sub> (and thus alkalinity) from surface waters and after dying transport it to the deep ocean where some of it redissolves. That which remains in sediments gets incorporated into the slow geological part of the carbon cycle from whence it is eventually replenished partly by input from rivers. The latter carry not only dissolved bicarbonate, but also suspended clay particles which release Ca<sup>2+</sup> by exchange with Na<sup>+</sup>. Thus the overall alkalinity of the ocean appears to have held fairly constant for at least the past 25 million years.

Local variations in seawater alkalinity are almost entirely due to variations in carbonate. This can be



To keep this diagram as simple (!) as possible, ion pairs such as  $CaOH^+$  and  $MgSO_4^+$  are not shown. The vertical line at  $pH = 8$  corresponds to normal seawater. The endpoint of an alkalinity titration occurs near  $pH 4.4$ . The broken lines correspond to supersaturation with calcite.

Figure 6: Log-C diagram showing the major acid-base components of seawater.

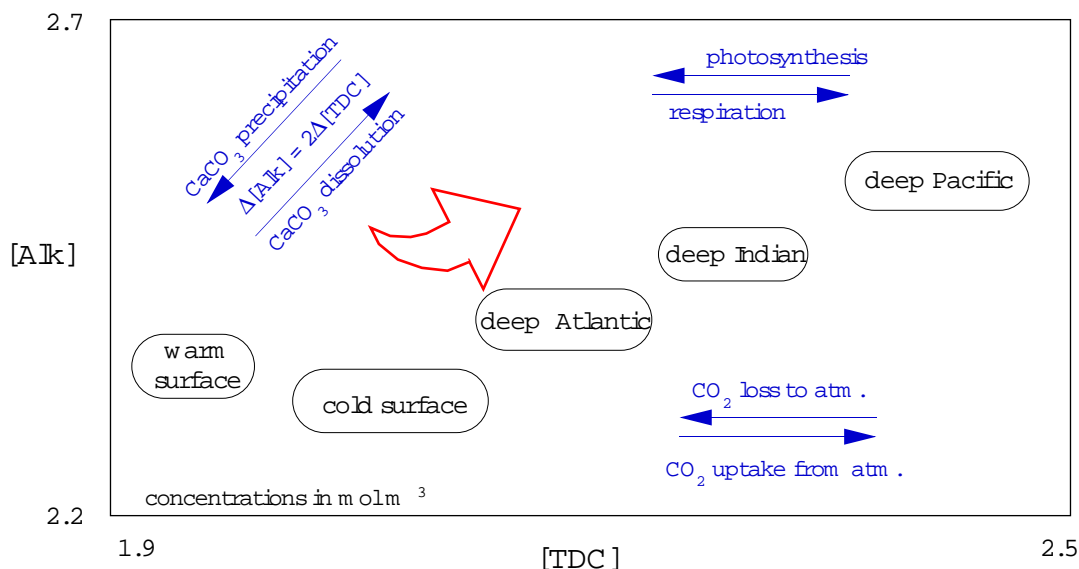


Figure 7: Trends in [Alk] and [TDC] in the major oceanic regions

seen from the charge balance of the major “strong” cations and anions:

$$[\text{Na}^+] + [\text{K}^+] + 2 [\text{Mg}^{2+}] + 2 [\text{Ca}^{2+}] = 606 \text{ mol m}^{-3}$$

$$[\text{Cl}^-] + 2 [\text{SO}_4^{2-}] + [\text{Br}^-] = 604 \text{ mol m}^{-3}$$

The deficit of negative charge is balanced by the alkalinity, of which almost all can be attributed to carbonates:

$$[\text{SID}] = [\text{Alk}] \approx [\text{HCO}_3^-] + [\text{carbonate}] = 2 \text{ mol m}^{-3}$$

Foraminifera and other organisms that precipitate  $\text{CaCO}_3$  shells remove two moles of strong cation charge per mole of  $\text{CaCO}_3$  formed, reducing [Alk] by *twice* the amount of carbon removed in this form. These same organisms also remove another mole of carbon to support their metabolism and the formation of soft tissues, so for every three carbon atoms withdrawn from the water, one  $\text{Ca}^{2+}$  is removed. The change in alkalinity is thus 2/3 the change in [TDC].

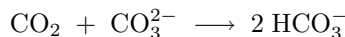
Intensive biomass production in the surface regions of the oceans, especially in the Atlantic, leaves this water depleted of phosphate and low in alkalinity and [TDC]. Some of this water sinks into the deep Atlantic from whence it circulates toward the Pacific. Along the way it picks up nutrients and carbonate from the detritus of dead organisms that continually rain down from the surface layers above. Some of this carbonate comes from the decomposition of the soft parts of the organisms, which releases mostly  $\text{CO}_2$ . Re-dissolution of  $\text{CaCO}_3$  skeletal parts also occurs, but to a smaller extent, releasing  $\text{CO}_3^{2-}$  which reacts with the  $\text{CO}_2$  to form  $\text{HCO}_3^-$ . Thus the Deep Pacific water contains more dissolved carbon but less  $\text{CO}_3^{2-}$  than other waters and as a consequence has a lower pH.

In its travels this water undergoes an increase in [TDC] by about 0.30 millimols/L, resulting in a rise in [Alk] by 2/3 as much, or about 0.20 millimols/L. The upwelling of this nutrient-rich water replenishes the upper parts of the ocean and is responsible for the economically important fishery along the western coasts of the Americas.



## 6.2 The oceans as a sink for atmospheric CO<sub>2</sub>

The question is often raised: how much of the increase in atmospheric CO<sub>2</sub> caused by the combustion of fossil fuel is taken up by the oceans? The reaction, of course, is



This occurs mainly in the wind-mixed upper 100 m of the ocean which can reach equilibrium with the atmosphere in about a year. Transport into the much larger deep ocean takes place on too slow a time scale (about 2000 years) to be important. It should also be pointed out that the ocean is not the only sink for carbon dioxide; weathering of rocks is another important process.

A quantity known as the Revelle buffer factor is often used to express the way in which the partial pressure of CO<sub>2</sub> in the atmosphere  $P$  depends on the total dissolved carbonate  $C_T$  in the ocean at constant alkalinity:

$$B = \frac{C_T}{P} \left( \frac{\partial P}{\partial C_T} \right)_{\text{Alk}} = \left( \frac{\partial \log P}{\partial \log C_T} \right)_{\text{Alk}} \quad (34)$$

Evaluation of this expression is straightforward but complicated (see [1], pg 145) and works out to approximately

$$B = \frac{C_T}{[\text{CO}_2] + [\text{CO}_3^{2-}]} + \dots \quad (35)$$

A more accurate expression would include the contribution of borate to the pH buffer capacity. The calculated and observed values<sup>3</sup> of  $B$  work out to about 14 at 2 °C, falling to 9 at 25 °C. (The negative temperature coefficient carries with it the disquieting implication of a runaway greenhouse effect.) Taking 10 as a representative value of  $B$ , this means that if the surface alkalinity remains constant, a change of 10 percent in the CO<sub>2</sub> content of the atmosphere will produce a 1 percent change in the concentration of total dissolved carbon in seawater.

It has been estimated<sup>4</sup> that the oceans actually absorb about half of the increase in atmospheric CO<sub>2</sub> that occurs over a period of 1-2 years. As  $C_T$  increases, so does  $B$ , suggesting that the absorptive capacity of the oceans should increase with time. Over a longer time scale, the ability of rock weathering and oceanic sediments to consume CO<sub>2</sub> far exceeds that of the ocean itself. The real question, then, is to what extent is the world likely to be affected by effects on the global climate that operate over a horizon of 50-500 years.

<sup>3</sup>Sundquist *et al*, 1979: Science 204:1203-1205)

<sup>4</sup>Broecker *et al*, 1979 Science 206:409-418

## References

- [1] BUTLER, JAMES N. *Carbon dioxide equilibria and their applications* 1982: Addison-Wesley This is the most complete and detailed treatment of the subject available, yet it is quite readable. *Contents:* Review of solubility and pH calculations, the basic equations, the alkalinity titration curve, solubility equilibria - calcium carbonate, applications to geochemistry and oceanography, engineering applications - water conditioning.
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- [4] MOREL, FRANÇOIS AND HERING, JANET *Principles and applications of aquatic chemistry* 1993: Wiley Written as a textbook, with many end-of-chapter problems.
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- [6] STUMM, WERNER AND MORGAN, JAMES *Aquatic chemistry* 3rd Ed 1995: Wiley This is the classic work on the subject, although perhaps a bit too rigorous to be useful as an introductory text. Chapter 4 of this book is devoted to the carbonate system.