INTRODUCTION TO CO$_2$ CHEMISTRY IN SEA WATER

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Monthly Average Carbon Dioxide Concentration
Data from Scripps CO₂ Program    Last updated November 2014
Effect of adding CO$_2$ to sea water

1. **Dissolves in the ocean**
   - CO$_2$ + H$_2$O $\rightleftharpoons$ HCO$_3^-$

2. **Reacts with water to form bicarbonate ion and hydrogen ion**
   - H$_2$O $\rightleftharpoons$ H$^+$ + OH$^-$
   - HCO$_3^-$

3. **Nearly all of that hydrogen ion reacts with carbonate ion to form more bicarbonate**
   - CO$_3^{2-}$ + H$^+$ $\rightarrow$ HCO$_3^-$

- Increase in dissolved CO$_2$ increases
- Decreases carbonate
- Increases bicarbonate
- Also hydrogen ion concentration increases
  - i.e., pH = $-\lg [H^+]$ decreases

And saturation state of calcium carbonate decreases

$$\Omega = \frac{[Ca^{+}][CO_3^{2-}]}{K_{sp}}$$

(a measure of how “easy” it is to form a shell)

CO$_2$ + CO$_3^{2-}$ + H$_2$O $\rightleftharpoons$ 2HCO$_3^-$
Multiple observed indicators of a changing global carbon cycle: (a) atmospheric concentrations of carbon dioxide (CO$_2$) from Mauna Loa (19°32´N, 155°34´W – red) and South Pole (89°59´S, 24°48´W – black) since 1958; (b) partial pressure of dissolved CO$_2$ at the ocean surface (blue curves) and in situ pH (green curves), a measure of the acidity of ocean water. Measurements are from three stations from the Atlantic (29°10´N, 15°30´W – dark blue/dark green; 31°40´N, 64°10´W – blue/green) and the Pacific (22°45´N, 158°00´W – light blue/light green) Oceans. — Figure from IPCC AR5.
The kinds of chemical questions we need to be able to answer

• If the CO$_2$ level in the atmosphere increases by 300 ppm, how much will the pH in the surface ocean change?

• What will be the consequent change in the saturation state of aragonite?

• Will this be the same all over the oceans? Why?

• How can I estimate the CO$_2$ composition of a sample of sea water?

• How should I modify the CO$_2$ composition of a sample of sea water to reach a desired target composition?
REQUIRES ACCESS TO VARIOUS “TOOLS”

- Understanding of acid-base (and especially CO$_2$) equilibria in sea water.
- Understanding of which CO$_2$ parameters in sea water are usually measured, and how.
- Access to suitable computational tools for the CO$_2$ system such as CO2calc.
- Access to suitable analytical equipment (and training) to make any CO$_2$ measurements desired.
1 The carbon dioxide system in seawater: equilibrium chemistry and measurements

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1.1 Introduction

The world’s oceans can be thought of as a dilute solution of sodium bicarbonate (together with other acid-base species at still lower concentrations) in a saltwater background. In the surface waters of the North Atlantic, for example, the concentration of total dissolved inorganic carbon (the sum of the concentrations of the three coexisting species: bicarbonate ion, carbonate ion, and unionised dissolved carbon dioxide) is only about 2 mmol kg\(^{-1}\). About 90% of this is present as bicarbonate ion, the proportion of carbonate ion is about a factor of 10 less (~10%), and that of unionised carbon dioxide yet another factor of 10 less (<1%). As a result of the equilibria between these various species (see below), seawater is buffered (weakly) with respect to changes in hydrogen ion (present at much lower concentrations: <10\(^{-8}\) µmol kg\(^{-1}\)).

Over the past twenty years, accurate measurement of the seawater carbon dioxide system has become a high priority for scientists who have worked to understand just how much of the carbon dioxide (CO\(_2\)) created by man’s activities has ended up in the ocean, where it is distributed, and how it has changed the chemistry of the oceans. The chemical changes associated with the increase of CO\(_2\) in the oceans are often referred to as ocean acidification. As we work to design suitable experiments to understand the biological and ecological consequences of such changes, it is important that the chemistry of CO\(_2\) be well characterised in the various laboratory experiments and field observations that are undertaken. Achieving this requires an understanding of the basic solution chemistry underlying ocean acidification, as well as of the relative merits of the various analytical techniques available to the investigator.

Unfortunately – from the point of view of someone desiring simplicity – in addition to carbon dioxide there are other acid-base systems in seawater that complicate things, particularly in systems that are not typical of the open surface ocean, with its low nutrient levels and relatively low amounts of dissolved organic material. The approach I shall take in this chapter is to introduce a somewhat simplified view of acid-base chemistry in seawater involving only the primary seawater acid-base systems: carbonic acid, boric acid and water. These will be discussed in some detail, and used to introduce the classical oceanographic analytical parameters for carbon dioxide studies in seawater: total dissolved inorganic carbon, total alkalinity, pH, and p(CO\(_2\)) – the partial pressure of carbon dioxide that is in equilibrium with a water sample (Box 1.1). The concept of calcium carbonate saturation state will also be introduced.

Once this basic seawater chemistry has been presented – and assimilated – it will be appropriate to revisit a number of these topics and to introduce further complexity, so as to clarify how these various concepts can be applied appropriately in the seawater systems that are of interest to investigators in ocean acidification.

Finally, I shall present a brief discussion of some of the current techniques available for the measurement of the various parameters of the seawater carbon dioxide system, and will indicate their advantages and disadvantages. The advantages and disadvantages of using alternate combinations of parameters to provide a complete description of the composition of a particular seawater sample will also be discussed.

As will become clear, at this time it is not as straightforward as one might wish to characterise the state of a particular seawater sample’s carbonate chemistry and to assign a well-constrained measurement uncertainty. Investigators who wish to do high quality work in ocean acidification, but who have little previous experience in seawater CO\(_2\) measurements, would do well to collaborate with a scientist with experience in this area and who has access to a working laboratory that can perform the necessary measurements with the required quality.
INTRODUCTION TO CO$_2$ EQUILIBRIA IN SEA WATER
COMPOSITION OF SEA WATER ($S = 35$)

Quantities in relation to 1 kg of sea water.
Acid-base species comprise a subset of the “minor constituents” present in seawater.

- $\text{HCO}_3^-$
- $\text{CO}_3^{2-}$
- $\text{OH}^-$
- $\text{SiO(OH)}_3^-$
- $\text{NH}_4^+$
- $\text{H}^+$
- $\text{CO}_2$
- $\text{H}_3\text{PO}_4$
- $\text{H}_2\text{PO}_4^-$
- $\text{B(OH)}_3$
- $\text{HF}$
- $\text{NH}_3$
- $\text{HPO}_4^{2-}$
- $\text{Si(OH)}_4$
- other acid/base species

Organic acids

Organic bases
ACID-BASE SPECIES COMPRIZE A SUBSET OF THE “MINOR CONSTITUENTS” PRESENT IN SEAWATER

Average ocean water; pH = 8; T = 18 °C; S = 35

\[
\begin{align*}
\text{HCO}_3^- & \quad \text{SiO(OH)}_3^- \\
\text{CO}_3^{2-} & \quad \text{NH}_4^+ \\
\text{OH}^- & \quad \text{organic acids} \\
\text{organic bases} & \quad \text{HF} \\
\text{B(OH)}_4^- & \quad \text{other acid/base species}
\end{align*}
\]
Average ocean water; pH = 8; t = 18 °C; S = 35

Acid-base species comprise a subset of the "minor constituents" present in seawater

\[
\begin{align*}
\text{HCO}_3^- & \quad \text{CO}_3^{2-} \\
\text{CO}_2 & \quad \text{H}_2\text{PO}_4^- \\
\text{OH}^- & \quad \text{B(OH)}_3 \\
\text{NH}_4^+ & \quad \text{H}_3\text{PO}_4 \\
\text{organic acids} & \quad \text{other acid/base species}
\end{align*}
\]
Average ocean water; pH = 8; t = 18 °C; S = 35

Acid-base species comprise a subset of the “minor constituents” present in seawater.

- $\text{HCO}_3^-$
- $\text{CO}_3^{2-}$
- $\text{H}_2\text{O}$
- $\text{H}_2\text{PO}_4^-$
- $\text{B(OH)}_3$
- $\text{SiO(OH)}_3^-$
- $\text{NH}_4^+$
- $\text{CO}_2$
- $\text{H}_3\text{PO}_4$
- $\text{H}_3\text{PO}_4$
- $\text{Si(OH)}_4$
- $\text{OH}^-$
- $\text{HF}$
- $\text{NH}_3$
- $\text{HPO}_4^{2-}$
- $\text{B(OH)}_4^-$
- organic acids
- organic bases
- other acid/base species

$344 \mu\text{mol kg}^{-1}$

$72 \mu\text{mol kg}^{-1}$
Average ocean water; pH = 8; \( t = 18 \) °C; \( S = 35 \)

**Acid-base species comprise a subset of the “minor constituents” present in seawater**

- \( \text{HCO}_3^- \)
- \( \text{CO}_3^{2-} \)
- \( \text{OH}^- \)
- \( \text{NH}_4^+ \)
- Other acid/base species

\[ \begin{align*}
\text{SiO(OH)}_3^- & \quad 3 \, \mu\text{mol kg}^{-1} \\
\text{CO}_2 & \\
\text{H}_2\text{O} & \\
\text{H}_2\text{PO}_4^- & \\
\text{H}_3\text{PO}_4 & \\
\text{B(OH)}_3 & \\
\text{HF} & \\
\text{NH}_3 & \quad 97 \, \mu\text{mol kg}^{-1} \\
\text{Si(OH)}_4 & \\
\text{B(OH)}_4^- & \\
\end{align*} \]
Average ocean water; pH = 8; t = 18 °C; S = 35

**Acid-base species comprise a subset of the “minor constituents” present in seawater**

- $\text{HCO}_3^-$
- $\text{CO}_3^{2-}$
- $\text{OH}^-$
- $\text{NH}_4^+$
- $\text{SiO(OH)}_3^-$
- $\text{H}^+$
- $\text{H}_2\text{O}$
- $\text{H}_2\text{PO}_4^-$
- $\text{H}_3\text{PO}_4$
- $\text{B(OH)}_3$
- $\text{HF}$
- $\text{HPO}_4^{2-}$
- $\text{PO}_4^{3-}$
- $\text{Si(OH)}_4$

Organic acids: $10^{-8} \text{ µmol kg}^{-1}$

Other acid/base species:
- $1.8 \text{ µmol kg}^{-1}$
- $2.10^{-2} \text{ µmol kg}^{-1}$
**Carbon Dioxide Equilibria in Sea Water**

**Gas solubility**
\[ \text{CO}_2 (g) = \text{CO}_2 (aq) \]

**Acid Dissociation**
\[ \text{CO}_2 + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^- \]
\[ \text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-} \]

**Equilibrium Constants**

- **Gas solubility equilibrium constant**
  \[ K_0 = \frac{[\text{CO}_2]}{x(\text{CO}_2) \cdot p} \]
  - Concentration of unionized \( \text{CO}_2 \) in sea water (mol kg\(^{-1}\))
  - Mole fraction of \( \text{CO}_2 \)
  - Equilibration pressure

- **Acid dissociation equilibrium constant**
  \[ K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \]
  - Total hydrogen ion concentration

- **Second dissociation of bicarbonate**
  \[ K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \]
Carbon dioxide equilibria in sea water

1. Dissolves in the ocean

\[ \text{CO}_2 \]

2. Reacts with water to form bicarbonate ion and hydrogen ion

\[ \text{H}_2\text{O} \rightarrow \text{H}^+ \] \[ \text{HCO}_3^- \]

3. Nearly all of that hydrogen ion reacts with carbonate ion to form more bicarbonate

\[ \text{CO}_3^{2-} \rightarrow \text{H}^+ \] \[ \text{HCO}_3^- \]

\[ \text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCO}_3^- \]

\[ K_0 = \frac{[\text{CO}_2]}{x(\text{CO}_2) \cdot p} \]

\[ K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \]

\[ \frac{1}{K_2} = \frac{[\text{HCO}_3^-]}{[\text{H}^+][\text{CO}_3^{2-}]} \]

\[ K_1 / K_2 = \frac{[\text{HCO}_3^-]^2}{[\text{CO}_2][\text{CO}_3^{2-}]} \]
**Carbon Dioxide Parameters in Sea Water**

- **Total Dissolved Inorganic Carbon**
  \[ C_T = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \]  
  **Units:** moles per kilogram of solution (usually µmol kg\(^{-1}\))

- **Total Hydrogen Ion Concentration (pH)**
  \[ \text{pH} = -\log ([\text{H}^+] / (\text{mol kg}^{-1})) \]  
  **Units:** pH is dimensionless; **but**, \([\text{H}^+]\), total hydrogen ion concentration is in moles per kilogram of solution

- **Partial Pressure of CO\(_2\)**
  (in air that is in equilibrium with the water sample)
  \[ p(\text{CO}_2) = x(\text{CO}_2) p = [\text{CO}_2] / K_0 \]  
  **Units:** pressure units (usually µatm)
CO$_2$ SYSTEM RELATIONSHIPS IN SEA WATER
At \( S = 35 \) and \( t = 18 \, ^\circ\text{C} \)

\[
\Omega(\text{arag}) = \frac{[\text{CO}_2] \cdot x(\text{CO}_2)}{\mu\text{atm}}
\]

\[
K_0 = \frac{[\text{CO}_2]}{x(\text{CO}_2) \cdot p}
\]

\[
\Omega(\text{arag}) = 1.0
\]

\[
\Omega(\text{arag}) = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{sp}(\text{arag})}
\]
**CO₂ SYSTEM RELATIONSHIPS IN SEA WATER**

At $S = 35$ and $t = 18$ °C

$$\frac{\rho \cdot x(\text{CO}_2)}{\mu \text{atm}}$$

$$K_1 / K_2 = \frac{[\text{HCO}_3^-]^2}{[\text{CO}_2][\text{CO}_3^{2-}]}$$

$\Omega(\text{arag}) = 1.0$
At $S = 35$ and $t = 18 \degree C$

\[
K_1 K_2 = \frac{[H^+]^2[C\text{O}_3^{2-}]}{[\text{CO}_2]}
\]

\[
\frac{[\text{CO}_3^{2-}]}{\mu\text{mol kg}^{-1}} = \frac{[\text{CO}_2]}{\mu\text{mol kg}^{-1}} \cdot x(\text{CO}_2)
\]

$\Omega(\text{arag}) = 1.0$
**IMPORTANT CONSEQUENCE OF CO$_2$ EQUILIBRIA**

- In a system at equilibrium, with both a gaseous and an aqueous phase, the state of the CO$_2$ system is described by a knowledge of the $p$(CO$_2$) in the gas phase, and of the four concentrations: [CO$_2$], [HCO$_3^-$], [CO$_3^{2-}$], and [H$^+$], in the aqueous phase.

- However, there are three equilibrium relationships between these various concentrations:

  
  \[
  K_0 = \frac{[CO_2]}{x(CO_2) \cdot p} \\
  K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]} \\
  K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}
  \]

- Hence there are only two degrees of freedom. This implies that only two of the aqueous concentrations can be varied independently of one another.
OTHER ACID-BASE SYSTEMS IN SEA WATER
**OTHER ACID-BASE SYSTEMS IN SEA WATER**

**Water Dissociation**

\[ \text{H}_2\text{O} = \text{H}^+ + \text{OH}^- \]

\[ K_w = [\text{H}^+][\text{OH}^-] \]

**Boric Acid Dissociation**

\[ \text{B(OH)}_3 + \text{H}_2\text{O} = \text{H}^+ + \text{B(OH)}_4^- \]

\[ K_B = \frac{[\text{H}^+][\text{B(OH)}_4^-]}{[\text{B(OH)}_3]} \]

**Total Dissolved Boron (depends on salinity)**

\[ B_T = [\text{B(OH)}_3] + [\text{B(OH)}_4^-] \]

For every other acid-base system considered, you need the total concentration and the equilibrium constant. The species concentrations can then be inferred from a knowledge of the pH.
TOTAL ALKALINITY

\[ A_T \approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+] \]

**UNITS:** moles per kilogram of solution (usually µmol kg\(^{-1}\))

1. What species are missing?
2. Why is this particular sum of species concentrations independent of temperature and pressure though each of the individual species contributions is itself a function of \( T \) and \( p \)?
3. A key aspect of total alkalinity: it does not change when \( \text{CO}_2 \) is added to or removed from sea water. Why?
Total alkalinity: The explicit conservative expression and its application to biogeochemical processes

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**Abstract**

Total alkalinity (TA) is one of the few measurable quantities that can be used together with other quantities to calculate concentrations of species of the carbonate system (CO\(_2\), HCO\(_3\)\(^-\), CO\(_3\)\(^2-\), H\(^+\), OH\(^-\)). TA and dissolved inorganic carbon (DIC) are conservative quantities with respect to mixing and changes in temperature and pressure and are, therefore, used in oceanic carbon cycle models. Thus it is important to understand the changes of TA due to various biogeochemical processes such as formation and remineralization of organic matter by microalgae, precipitation and dissolution of calcium carbonate. Unfortunately deriving such changes from the common expression for TA in terms of concentrations of non-conservative chemical species (HCO\(_3\)\(^-\), CO\(_3\)\(^2-\), B(OH)\(_4\)\(^-\), H\(^+\), OH\(^-\), etc.) is rarely obvious.
IMPLICATIONS FOR THE DEGREES OF FREEDOM FOR ACID-BASE SYSTEMS IN SEAWATER

• We stated earlier that there are only two degrees of freedom and that only two of the aqueous concentrations of the CO$_2$ species can be varied independently of one another.

• However, for each additional acid-base system (except water) that is added in, there are two additional species concentrations and one equilibrium relationship. Thus there will be an additional degree of freedom for each new acid/base pair.

• Furthermore, one does not have to limit oneself to simple species concentrations when thinking of “concentrations” that can be varied independently. It also applies to combinations of species concentrations such as $C_T$ or $A_T$. 
COMPUTER PROGRAMS EXIST FOR THESE CALCULATIONS

- Provide built in data for the various equilibrium constants and for total concentrations such as boron that are proportional to salinity.

- Allow some additional acid-base information to be added (e.g. total phosphate and/or total silicate concentrations)

- Allow calculation of CO₂ speciation (typically from 2 analytical parameters, salinity & temperature)
Florida Shelf Ecosystems Response to Climate Change Project

CO2calc: A User-Friendly Seawater Carbon Calculator for Windows, Mac OS X, and iOS (iPhone)

Can use any two (or more) of these parameters to describe the CO$_2$ system in a sea water sample.

Mathematically, all choices should be equivalent.

In practice that is not the case. Every one of these terms is an experimental quantity with an associated uncertainty. These uncertainties propagate through the calculations resulting in uncertainties in the various calculated values.

In addition to uncertainties in the measured CO$_2$ parameters, there are also uncertainties in the various equilibrium constants, and in the total concentrations of other acid-base systems such as boron, etc.

(Also, the expression used for alkalinity may be incomplete.)
As yet it is not straightforward to carry out a rigorous consideration of such uncertainties. Thus they are often – mistakenly – ignored.
IMPLICATIONS FOR THE “ACIDIFICATION” OF SEA WATER
ACIDIFICATION TO pH 7.3

At $S = 35$ and $t = 18 \, ^\circ\text{C}$

$$\frac{\rho \cdot x(\text{CO}_2)}{\mu\text{atm}}$$

$$K_1 / K_2 = \frac{[\text{HCO}_3^-]^2}{[\text{CO}_2][\text{CO}_3^{2-}]}$$

**Initial Conditions:**

- $A_T = 2300 \, \mu\text{mol kg}^{-1}$
- $\text{pH} = 8.2$

**Graph:**

- $x$-axis: $[\text{CO}_2^-]/\mu\text{mol kg}^{-1}$
- $y$-axis: $[\text{CO}_3^{2-}]/\mu\text{mol kg}^{-1}$
- $\Omega(\text{arag}) = 1.0$
ACIDIFICATION TO pH 7.3 (BY ADDITION OF CO₂)

At $S = 35$ and $t = 18$ °C

**Initial Conditions:**
- $\Delta C_T \approx +360 \, \mu\text{mol kg}^{-1}$
- $A_T = 2300 \, \mu\text{mol kg}^{-1}$
- pH = 8.2

**Final Conditions:**
- $p(\text{CO}_2) = 2630 \, \mu\text{atm}$
- $[\text{CO}_3^{2-}] = 37 \, \mu\text{mol kg}^{-1}$
- $\Omega(\text{arag}) = 0.57$
- $\Omega(\text{arag}) = 1.0$
ACIDIFICATION TO pH 7.3 (BY ADDITION OF HCl)

At $S = 35$ and $t = 18$ °C

**INITIAL CONDITIONS:**
$A_T = 2300 \ \mu$mol kg$^{-1}$
$pH = 8.2$

$\Delta A_T \approx -358 \ \mu$mol kg$^{-1}$

$\Delta C_T \approx +365 \ \mu$mol kg$^{-1}$

**FINAL CONDITIONS:**
$p(CO_2) = 2630 \ \mu$atm
$[CO_3^{2-}] = 37 \ \mu$mol kg$^{-1}$
$\Omega(arag) = 0.57$

$p(CO_2) = 2220 \ \mu$atm
$[CO_3^{2-}] = 31 \ \mu$mol kg$^{-1}$
$\Omega(arag) = 0.48$
WHAT HAPPENS AT A DIFFERENT TEMPERATURE?

INITIAL CONDITIONS: 
\[ A_T = 2300 \, \mu \text{mol kg}^{-1} \]
\[ p(\text{CO}_2) = 280 \, \mu \text{atm} \]

FINAL CONDITIONS: 
\[ A_T = 2300 \, \mu \text{mol kg}^{-1} \]
\[ p(\text{CO}_2) = 1500 \, \mu \text{atm} \]
INITIAL CONDITIONS:
$A_T = 2300 \text{ µmol kg}^{-1}$
$p(CO_2) = 280 \text{ µatm}$

FINAL CONDITIONS:
$A_T = 2300 \text{ µmol kg}^{-1}$
$p(CO_2) = 1500 \text{ µatm}$
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<th>S = 35</th>
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<td>( \Delta C_T )</td>
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IMPLICATIONS OF CO$_2$ EQUILIBRIA FOR DESIGN OF OCEAN ACIDIFICATION EXPERIMENTS

- Only two of the concentrations of the aqueous CO$_2$ species can be varied independently of one another. Thus we cannot design perfect experiments to study organismal physiology, however we only need to control two CO$_2$ parameters.

- If you know what sea water composition you have to start with, and know the composition you want to get to, it is often simpler to think about the changes as if they occur in total alkalinity and in total dissolved inorganic carbon.

- In many systems, it is not convenient to alter the sea water alkalinity to a target value, and one just uses the alkalinity of the source sea water as is.

- It is often best to control pH – by varying $p$(CO$_2$). This is less demanding of temperature control than monitoring $p$(CO$_2$).
Any questions?

OK – Time for coffee!

I DON'T BELIEVE IN GLOBAL WARMING