Global Carbon Cycle
AOSC 433/633 & CHEM 433/633
Ross Salawitch & Tim Canty

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2013

Goals for today:
• Overview of the Global Carbon Cycle, “scratching below the surface” of the reading material
• Land and ocean uptake of CO₂
• Connect to prior lectures: ΔF & ΔT, the “CO₂ response function”, as well as glacial CO₂

Positive Feedback:
climate responds to an initial perturbation in a manner that amplifies the perturbation

Earth’s orbit and CO₂ / CH₄:
change in Earth’s orbit leads to more sunlight during NH summer this warms the high-latitude ocean, causing CO₂ to be released higher CO₂ leads to additional warming because CO₂ is a GHG higher T melts permafrost, releasing trapped CH₄ higher CH₄ contributes to even more additional warming
Modern CO₂ Record

Δ (CO₂) years 1959 to 2012 =
ΔF =
ΔTEXPECTED =

ΔTACTUAL ≈

CO₂ Essentially Inert in the Atmosphere

Decreasing oxidation number (reduction reactions)

<table>
<thead>
<tr>
<th>-4</th>
<th>0</th>
<th>+2</th>
<th>+4</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ Methane</td>
<td>CH₂O Formaldehyde</td>
<td>CO Carbon Monoxide</td>
<td>CO₂ Carbon dioxide</td>
</tr>
</tbody>
</table>

Increasing oxidation number (oxidation reactions)

Oxidation state represents number of electrons:
added to an element (negative #) or removed from an element (positive #)

\[ \overset{-1}{\text{O}} = \overset{0}{\text{C}} = \overset{+1}{\text{O}} \]

C in CO₂: has donated two electrons to each oxygen atom,
completing the L shell of electrons & resulting
in an electron configuration analogous to helium

CO₂, the most oxidized form of carbon, is essentially inert in the atmosphere.
Yet, many atmospheric scientists focus their research on the “global carbon cycle”.

Legacy of Charles Keeling, Scripps Institution of Oceanography, La Jolla, CA
http://www.esrl.noaa.gov/gmd/ccgg/trends

Copyright © 2013 University of Maryland.
This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch or Tim Canty.
Modern CO₂ Record

\[ \Delta (\text{CO}_2) \text{ years 1959 to 2011} = 75.6 \text{ ppm} \]

\[ \Delta \text{ mass of C} = 75.6 \text{ ppm} \times \frac{10^{-6}}{\text{ppm}} \times 5.2 \times 10^{21} \text{gm} \times \frac{12 \text{ gm C/mole}}{29 \text{ gm/mole}} \]

\[ = 1.63 \times 10^{17} \text{gm C} \]

\[ = 1.63 \times 10^{17} \text{gm C} \times 10^{-6} \text{ton/gm} \]

\[ = 1.63 \times 10^{11} \text{tons C} \]

\[ = 163 \times 10^9 \text{tons C} = 163 \text{ Gtons of C} \]

Legacy of Charles Keeling, Scripps Institution of Oceanography, La Jolla, CA
http://www.esrl.noaa.gov/gmd/ccgg/trends

Copyright © 2013 University of Maryland.
This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch or Tim Canty.

Global Carbon Cycle

Fossil fuel emissions, 1959 to 2011 = 296 Gt C

\[ \Delta (\text{CO}_2), \text{1959 to 2011} = 162 \text{ Gt C} \]

~55% of carbon emitted remains in the atmosphere
Houghton reading states ~45%
"about half" will suffice 😊

Rest goes to either?
Human Release of Carbon

Human activity is presently releasing about 9 Gt (giga tons) or $9,000,000,000$ (9 \times 10^9) tons of Carbon per year.

How much is 9 Gt of carbon ?!?
13CO2 Time Evolution: “Fingerprint” of Fossil Fuel Burning

Atmospheric CO2 since ~1860

Why did CO2 start to rise?

Figure 3.5, Chemistry in Context
Figure 3.3 (a) Fossil carbon emissions (based on statistics of fossil fuel and cement production) and estimates of global reservoir changes: atmosphere (deduced from direct observations and ice core measurements), ocean (calculated with the Geophysical Fluid Dynamics Laboratory (GFDL), University of Princeton, ocean carbon model) and net terrestrial biosphere (calculated as remaining imbalance) from 1840 to 1990. The calculation implies that the terrestrial biosphere was a net source to the atmosphere prior to 1940 (negative values) and has been a net sink since about 1960.

Global Carbon Cycle

Figure 3.1 The global carbon cycle, showing the carbon stocks in reservoirs (in Gt) and carbon flows (in Gt year⁻¹) relevant to anthropogenic perturbation as annual averages over the decade from 1989 to 1998. Net ocean uptake of the anthropogenic perturbation equals the net air/sea input plus runoff minus sediment. The units are thousand millions of tonnes or gigatonnes (Gt).
CO₂ Is Long Lived

Table TS.2. Lifetimes, radiative efficiencies and direct (except for CH₄) global warming potentials (GWP) relative to CO₂. (Table 2.14)

<table>
<thead>
<tr>
<th>Industrial Designation or Common Name (years)</th>
<th>Chemical Formula</th>
<th>Lifetime (years)</th>
<th>Radiative Efficiency (W m⁻² ppb⁻¹)</th>
<th>Global Warming Potential for Given Time Horizon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>See below</td>
<td>1.4 × 10⁻⁵</td>
<td>1 1 1 1</td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>12</td>
<td>3.7 × 10⁻⁴</td>
<td>21 72 25 7.6</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>N₂O</td>
<td>114</td>
<td>3.03 × 10⁻³</td>
<td>310 289 298 133</td>
</tr>
</tbody>
</table>

Notes:
1. SAR refers to the IPCC Second Assessment Report (1995) used for reporting under the UNFCCC.
2. The CO₂ response function used in this report is based on the revised version of the Bern carbon cycle model used in Chapter 10 of this report (Bern2.5CC, Joos et al. 2001) using a background CO₂ concentration value of 378 ppm. The decay of a pulse of CO₂ with time t is given by
   \[ a₂ + \frac{1}{\tau} a₁ e^{-\frac{t}{\tau}} \]
   where \( a₀ = 0.217, a₁ = 0.259, a₂ = 0.338, \tau₁ = 172.9 \text{ years}, \tau₂ = 18.51 \text{ years}, \) and \( \tau₃ = 1.186 \text{ years, for } t < 1.000 \text{ years.} \)
3. The radiative efficiency of CO₂ is calculated using the IPCC (1990) simplified expression as revised in the TAR, with an updated background concentration value of 378 ppm and a perturbation of +1 ppm (see Section 2.10.2).
4. The perturbation lifetime for CH₄ is 12 years as in the TAR (see also Section 7.4). The GWP for CH₄ includes indirect effects from enhancements of ozone and stratospheric water vapor (see Section 2.10).

from IPCC 2007 “Physical Science Basis”

Copyright © 2013 University of Maryland.
This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch or Tim Cancy.
CO₂ is long lived: society must reduce emissions soon or we will be committed to dramatic, future increases!

Curve that levels off at ~560 ppm has emissions peaking ~2030
Less than 20 years from now!

Global Carbon Cycle

Where is the CO₂ being sequestered?

During the 1990s, humans released ~6 Gt C/yr.

If ~50% stayed in atmosphere, then 0.5 \times 6 \text{ Gt C/yr} \approx 3.0 \text{ Gt C/yr} went to land and oceans

Ocean uptake estimated to be:

- \delta^{13}C isotopic fractionation [Gruber and Keeling, 2001]
- Minute changes in atmospheric O₂/N₂ ratio [Bopp et al., 2002]
- In situ measurements atmospheric CO₂, 46 surface sites [Peylin et al., 2002]
- Ship board measurements of ΔpCO₂ across air-sea interface [Takahashi et al., 1999]
Global Carbon Cycle

Where is the CO₂ being sequestered?
During the 1990s, humans released ~6 Gt C/yr.
If ~50% stayed in atmosphere, then 0.5 × 6 Gt C/yr = 3.0 Gt C/yr went to land and oceans

**Land uptake estimated to be:**

- 0.7 ± 0.7 GtC/yr for North America
- 0.5 ± 0.8 GtC/yr for Europe
- 1.2 ± 0.8 GtC/yr for North Asia
  [Bousquet *et al.*, 2000]
- 0.5 GtC/yr for continental United States
  [Pacala *et al.*, 2001]
- 1.8 Gt for North America
- 2.4 Gt for continental United States
- 0.5 Gt for North Asia
- 0.7 GtC/yr for Europe
- 1.2 GtC/yr for North Asia
- 0.5 Gt for continental United States

1.7 ± 0.5 GtC/yr for North America
0.1 ± 0.6 GtC/yr for Eurasia/North Africa
[Fan *et al.*, 1992]

Inferring CO₂ Uptake Based on Δ(O₂)

**Bookkeeping according to this study:**
- Atmospheric Release: 30.0 ppm (66 Gt)
- Atmospheric Increase: 15.1 ppm (~50% airborne fraction)
- Land Uptake: 6.8 ppm (46% of uptake)
- Ocean Uptake: 8.1 ppm (54% of uptake)

[Figure 3.4] Partitioning of fossil fuel carbon dioxide uptake using oxygen measurements. Shown is the relationship between changes in carbon dioxide and oxygen concentrations. Observations are shown by solid circles and triangles. The arrow labeled 'fossil fuel burning' denotes the effect of the combustion of fossil fuels based on the O₂:CO₂ stoichiometric ratio associated with these processes, defining the slopes of the respective arrows.
Uptake of Atmospheric \( \text{CO}_2 \) by Trees (Land Sink)

Land sink:

As \( \text{CO}_2 \) ↑, photosynthesis (all things being equal) will increase. Known as the "\text{CO}_2\ "fertilizer" effect

Difficult to quantify because?

The carbon dioxide ‘fertilisation’ effect

An important positive effect of increased carbon dioxide (\( \text{CO}_2 \)) concentrations in the atmosphere is the boost to growth in plants given by the additional \( \text{CO}_2 \). Higher \( \text{CO}_2 \) concentrations stimulate photosynthesis, enabling the plants to fix carbon at a higher rate. This is why in glasshouses additional \( \text{CO}_2 \) may be introduced artificially to increase productivity. The effect is particularly applicable to what are called C3 plants (such as wheat, rice and soya bean), but less so to C4 plants (for example, maize, sorghum, sugar-cane, millet and many pasture and forage grasses). Under ideal conditions it can be a large effect; for C3 crops under doubled \( \text{CO}_2 \), an average of +30%.\(^{37}\)

Uptake of Atmospheric \( \text{CO}_2 \) by Trees (Land Sink)

Land sink: relatively short lived reservoir

- In this model, future water stress due to climate change eventually limits plant growth
- Feedbacks between climate change and plants lead to several 100 ppm additional \( \text{CO}_2 \) by end of century

![Graph showing projected future \( \text{CO}_2 \) and \( T \) for a single fossil fuel carbon emission scenario](image)

**Figure 3.5** Illustrating the possible effects of climate feedbacks on the carbon cycle. Results are shown of the changing budgets of carbon

Page 41, Houghton

Cox et al., *Nature*, 2000
Uptake of Atmospheric CO$_2$ by Trees (Land Sink)

Land sink: relatively short lived reservoir

- IPCC 2007 did not consider carbon cycle feedbacks in latest assessment, as there is no scientific consensus on the direction (much less magnitude) of this effect!

Intercomparison of 250 years of simulated carbon uptake by land and the resulting increase in atmospheric CO$_2$ by 11 coupled carbon cycle – climate models, using an identical prescribed fossil fuel emission scenario (Friedlingstein et al., 2006)

Uptake of Atmospheric CO$_2$ by Oceans

Acidity of pure water is 7. This means [H$^+$] = 10$^{-7}$ moles/liter or 10$^{-7}$ M.

What is acidity of water in equilibrium with atmospheric CO$_2$?
Uptake of Atmospheric CO$_2$ by Oceans

When CO$_2$ dissolves:

Henry’s law governs ratio of CO$_2$(aq) to pCO$_2$,
where pCO$_2$ is the atmospheric CO$_2$ mixing ratio: $CO_2(aq) = \alpha \ pCO_2$

The following aqueous phase equilibrium reactions occur:

\[
CO_2(aq) + H_2O \leftrightarrow HCO_3^- + H^+
\]

\[
H^+ + CO_3^{2-} \leftrightarrow HCO_3^-
\]

If water is exposed to higher levels of pCO$_2$, leading to larger CO$_2$(aq),
the following net reaction is considered to occur:

\[
CO_2(aq) + CO_3^{2-} + H_2O \rightarrow 2 HCO_3^-
\]

As CO$_2$ dissolves, CO$_3^{2-}$ is converted to HCO$_3^-$

Also, the following aqueous equilibrium is maintained:

\[
K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = 4.7 \times 10^{-11} \text{ M at 298 K}
\]

So … as CO$_2$(aq) rises due to rising atmospheric CO$_2$
CO$_3^{2-}$ will fall and [HCO$_3^-$] will rise and therefore …

[H$^+$] must **RISE** (for above equilibrium to be maintained)

---

Uptake of Atmospheric CO$_2$ by Oceans

Acidity of actual ocean is much more complex than pure rainwater: *ocean is slightly basic*

Dominant **cations** are Na$^+$, K$^+$, Mg$^{2+}$ and Ca$^{2+}$

Most common **anions** are Cl$^-$, Br$^-$, and SO$_4^{2-}$

Positive charge of cations *slightly larger* than negative charge of anions:

difference is called “**Ocean Alkalinity**” and is balanced by HCO$_3^-$ and CO$_3^{2-}$

\[
[\text{Alk}] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}]
\]

Atmospheric CO$_2$, CO$_2$(aq), HCO$_3^-$, CO$_3^{2-}$ follow same relation as given on prior slide.

We define Ocean Carbon (traditionally DIC for dissolved inorganic carbon) as:

**Ocean Carbon** $[\Sigma \ CO_2] = [CO_2(aq)] + [HCO_3^-] + [CO_3^{2-}]$

and note that the relation between Ocean Carbon and its components depends on

temperature, alkalinity, salinity (saltiness), and atmospheric CO$_2$

**The mathematics relating ocean acidity to pCO$_2$, T & Alkalinity**

*is given on Extra Slide #3*
Uptake of Atmospheric CO₂ by Oceans

When CO₂ dissolves:

\[
\text{Net: } \text{CO}_2^{\text{aq}} + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow 2 \text{HCO}_3^{-}
\]

<table>
<thead>
<tr>
<th>Atmospheric CO₂</th>
<th>280 ppm</th>
<th>385 ppm</th>
<th>560 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Industrial</td>
<td></td>
<td></td>
<td>2 × Pre-Indus.</td>
</tr>
<tr>
<td>Ocean Carbon</td>
<td>2020 ×10⁻⁶ M</td>
<td>2070 ×10⁻⁶ M</td>
<td>2122 ×10⁻⁶ M</td>
</tr>
<tr>
<td>[HCO₃⁻]</td>
<td>1772 ×10⁻⁶ M</td>
<td>1865 ×10⁻⁶ M</td>
<td>1957 ×10⁻⁶ M</td>
</tr>
<tr>
<td>[CO₂(aq)]</td>
<td>9.1 ×10⁻⁶ M</td>
<td>12.6 ×10⁻⁶ M</td>
<td>18.2 ×10⁻⁶ M</td>
</tr>
<tr>
<td>[CO₃²⁻]</td>
<td>239 ×10⁻⁶ M</td>
<td>193 ×10⁻⁶ M</td>
<td>146 ×10⁻⁶ M</td>
</tr>
<tr>
<td>pH</td>
<td>8.32</td>
<td>8.20</td>
<td>8.06</td>
</tr>
</tbody>
</table>

Revelle Factor = \( \frac{\Delta \text{Atmos}_{\text{CO}_2}/\langle \text{Atmos}_{\text{CO}_2}\rangle_{\text{AVERAGE}}}{\Delta \text{Ocean Carbon}/\langle \text{Ocean Carbon}\rangle_{\text{AVERAGE}}} \)

= \( \frac{105/332.5}{50/2045} \) = 12.9 (from pre-industrial to present-day CO₂)

= \( \frac{175/472.5}{52/2096} \) = 14.9 (from present-day to 2 × pre-industrial CO₂)

**Uptake of Atmospheric CO₂ by Oceans**

\( \Delta \text{Ocean Carbon}/\langle \text{Ocean Carbon}\rangle_{\text{AVERAGE}} \) used to be \( \frac{\Delta \text{Atmos}_{\text{CO}_2}/\langle \text{Atmos}_{\text{CO}_2}\rangle_{\text{AVERAGE}}}{12.9} \)

or \( 0.078 \times \frac{\Delta \text{Atmos}_{\text{CO}_2}/\langle \text{Atmos}_{\text{CO}_2}\rangle_{\text{AVERAGE}}}{12.9} \)

\( \Delta \text{Ocean Carbon}/\langle \text{Ocean Carbon}\rangle_{\text{AVERAGE}} \) now \( \frac{\Delta \text{Atmos}_{\text{CO}_2}/\langle \text{Atmos}_{\text{CO}_2}\rangle_{\text{AVERAGE}}}{14.9} \)

or \( 0.067 \times \frac{\Delta \text{Atmos}_{\text{CO}_2}/\langle \text{Atmos}_{\text{CO}_2}\rangle_{\text{AVERAGE}}}{14.9} \)

**Capacity of ocean to absorb carbon decreases over time!**
Revelle Factor

In 1957, Revelle co-authored a paper with Hans Suess that suggested Earth's oceans would absorb excess carbon dioxide generated by humanity in the future at a rate less than predicted…

Revelle and Suess described the "buffer factor", now known as the "Revelle factor", which is the resistance to atmospheric carbon dioxide being absorbed by the ocean surface layer posed by bicarbonate chemistry. Essentially, to enter the ocean, carbon dioxide gas has to partition into one of the components of carbonic acid: carbonate ion ($\text{CO}_3^{2-}$), bicarbonate ion ($\text{HCO}_3^-$), or carbonic acid ($\text{H}_2\text{CO}_3$). This chemistry limits how fast atmospheric carbon dioxide can enter the surface ocean, with the rate limiting reactant, carbonate ion, decreasing as atmospheric CO$_2$ rises.

Al Gore mentions Roger Revelle as a "personal inspiration" in a segment of *An Inconvenient Truth*


---

Uptake of Atmospheric CO$_2$ by Oceans

– Solubility Pump:
  a) More CO$_2$ can dissolve in cold polar waters than in warm equatorial waters. As major ocean currents (e.g. the Gulf Stream) move waters from tropics to the poles, they are cooled and take up atmospheric CO$_2$
  b) Deep water forms at high latitude. As deep water sinks, ocean carbon ($\Sigma$CO$_2$) accumulated at the surface is moved to the deep ocean interior.

– Biological Pump:
  a) Ocean biology limited by availability of nutrients such as NO$_3^-$, PO$_4^{3-}$, and Fe$^{2+}$ & Fe$^{3+}$. Ocean biology is never carbon limited.
  b) Detrital material "rains" from surface to deep waters, contributing to higher CO$_2$ in intermediate and deep waters

[http://science.nasa.gov/headlines/y2004/05mar_arctic.htm](http://science.nasa.gov/headlines/y2004/05mar_arctic.htm)
Uptake of Atmospheric CO$_2$ by Oceans

− Solubility Pump:
  a) More CO$_2$ can dissolve in cold polar waters than in warm equatorial waters. As major ocean currents (e.g. the Gulf Stream) move waters from tropics to the poles, they are cooled and take up atmospheric CO$_2$
  b) Deep water forms at high latitude. As deep water sinks, ocean carbon ($\Sigma$CO$_2$) accumulated at the surface is moved to the deep ocean interior.

− Biological Pump:
  a) Ocean biology limited by availability of nutrients such as NO$_3^-$, PO$_4^{3-}$, and Fe$^{2+}$ & Fe$^{3+}$. Ocean biology is never carbon limited.
  b) Detrital material "rains" from surface to deep waters, contributing to higher CO$_2$ in intermediate and deep waters

Connection to Glacial CO$_2$

**Glacial-to-interglacial variations in the carbon isotopic composition of atmospheric CO$_2$**

Bruno D. Marino, Michael B. McElroy, Ross J. Salawitch & W. Geoffrey Spaulding

Lower concentrations of CO$_2$ during glacial times are attributed to an increased supply of nutrients to the surface of the low-latitude ocean, and to biological and physical influences resulting in an increase in the abundance of CO$_3^{2-}$ in WSW

See [http://www.nature.com/nature/journal/v357/n6378/abs/357461a0.html](http://www.nature.com/nature/journal/v357/n6378/abs/357461a0.html)

GLACIAL-INTERGLACIAL CO$_2$ CHANGE: **PALEOCEANOGRAPHY**, VOL.5, THE IRON HYPOTHESIS

John H. Martin

In contrast, atmospheric dust Fe supplies were 50 times higher during the last glacial maximum (LGM). Because of this Fe enrichment, phytoplankton growth may have been greatly enhanced, larger amounts of upwelled nutrients may have been used, and the resulting stimulation of new productivity may have contributed to the LGM drawdown of atmospheric CO$_2$ to levels of less than 200 ppm. Background information and arguments in support of this hypothesis are presented.

See [http://www.agu.org/journals/pa/v005/i001/PA005i001p00001](http://www.agu.org/journals/pa/v005/i001/PA005i001p00001)
Uptake of Atmospheric CO₂ by Oceans

Future ocean uptake of atmospheric CO₂ will lead to **ocean acidification**

Bad news for ocean dwelling organisms that precipitate shells (basic materials)

---

**THE RAGGED FUTURE OF ARAGONITE**

Diminishing pH levels will weaken the ability of certain marine organisms to build their hard parts and will be felt soonest and most severely by those creatures that make those parts of aragonite, the form of calcium carbonate that is most prone to dissolution. The degree of threat will vary regionally.

---

**Extra Slide 1**

**Carbon Water Chemistry**

Acidity of pure water is 7. This means \([H^+] = 10^{-7}\) moles/liter or \(10^{-7}\) M.

What is acidity of water in equilibrium with atmospheric CO₂?

\[
[CO_2(aq)] = H_{CO_2} \quad p_{CO_2} = 3.4 \times 10^{-2} \text{ M} / \text{atm} \quad p_{CO_2}
\]

For CO₂ = 390 ppm:

\[
[CO_2(aq)] = 3.4 \times 10^{-2} \text{ M} / \text{atm} \quad 3.9 \times 10^{-4} \text{ atm} = 1.326 \times 10^{-5} \text{ M}
\]

First equilibrium between CO₂, HCO₃⁻ (bicarbonate), and H⁺

\[
CO_2(aq) + H_2O \leftrightarrow HCO_3^- + H^+ \\
K_1 = \frac{[HCO_3^-][H^+]}{[CO_2(aq)]} = 4.3 \times 10^{-7} \text{ M} \text{ (at 298 K)}
\]

Second equilibrium between CO₃²⁻ (carbonate), HCO₃⁻, and H⁺

\[
H^+ + CO_3^{2-} \leftrightarrow HCO_3^- \\
K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = 4.7 \times 10^{-11} \text{ M} \text{ (at 298 K)}
\]

Can solve if we assume charge balance: \([H^+] = [HCO_3^-] + 2 [CO_3^{2-}]\)

- or - by taking a short-cut (see next slide)
Carbon Water Chemistry

Acidity of pure water is 7. What is acidity of water in equilibrium with atmospheric CO$_2$?

Shortcut:

\[ [\text{CO}_2(\text{aq})] = H_{\text{CO}_2} \quad p_{\text{CO}_2} = 3.4 \times 10^{-2} \text{ M} / \text{atm} \quad p_{\text{CO}_2} = 1.326 \times 10^{-5} \text{ M} \quad \text{for present atmosphere} \]

\[ [H^+] \quad [\text{HCO}_3^-] = K_1 \quad [\text{CO}_2(\text{aq})] = 4.3 \times 10^{-7} \text{ M} \times 1.326 \times 10^{-5} \text{ M} = 5.70 \times 10^{-12} \text{ M}^2 \]

*Assume* charge balance is primarily between [H$^+$] and [HCO$_3^-$]:

i.e., that [H$^+$] $\approx$ [HCO$_3^-$] and that both are $\gg$ [CO$_3^{2-}$]

\[ [H^+] \quad [H^+] = 5.70 \times 10^{-12} \text{ M}^2 \Rightarrow [H^+] = 2.388 \times 10^{-6} \text{ M} \]

\[ pH = - \log_{10} [H^+] = 5.6 \quad (390 \text{ ppm, } 298 \text{ K}) \]

Is the *assumption* justified?

\[ [\text{CO}_3^{2-}] = K_2 \frac{[\text{HCO}_3^-]}{[H^+]} \approx 4.7 \times 10^{-11} \text{ M} \]

[H$^+$] & [HCO$_3^-$] are both $\approx 2.4 \times 10^{-6} \text{ M}$ which is $\gg 4.7 \times 10^{-11} \text{ M}$

Ocean Acidity

As noted in class, the actual ocean is basic. The net charge from a series of cations (positively charged ions) and minor anions (negatively charged ions) is balanced by the total negative charge of the bicarbonate and carbonate ions. We write:

\[ [\text{Alk}] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] = [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] - [\text{Cl}^-] - [\text{Br}^-] - 2[\text{SO}_4^{2-}] + ... \]

where Alk stands for Alkalinity

Henry’s Law and the equations for the first and second dissociation constants yield:

\[ p_{\text{CO}_2(\text{vmr})} = \frac{[\text{CO}_2(\text{aq})]}{\alpha} \quad K_1 = \frac{[\text{HCO}_3^-][H^+]}{[\text{CO}_2(\text{aq})]} \quad K_2 = \frac{[\text{CO}_3^{2-}][H^+]}{[\text{HCO}_3^-]} \]

The three equations above can be re-arranged to yield:

\[ p_{\text{CO}_2(\text{vmr})} = \frac{K_2}{\alpha K_1} \left( \frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} \right)^2 \]

If we substitute [HCO$_3^-$] = Alk – 2 [CO$_3^{2-}$] into the eqn above, we arrive at a quadratic eqn for [CO$_3^{2-}$] as a function of pCO$_2$ and Alk. Note that $\alpha$, $K_1$, and $K_2$ vary as a function of temperature (T) and ocean salinity (S) (http://en.wikipedia.org/wiki/Salinity)

If T, Alk, & S are specified, it is straightforward to solve for [CO$_3^{2-}$] from the quadratic eqn.

Values for [CO$_2$(aq)], [HCO$_3^-$], and [H$^+$] are then found from Henry’s law & the dissoeqns.

Finally, Ocean Carbon is found from [CO$_2$(aq)] + [HCO$_3^-$] + [CO$_3^{2-}$].

Numerical values on the slides entitled “Uptake of Atmospheric CO$_2$ by Oceans” were found in this manner, using Fortran program http://www.atmos.umd.edu/~rjs/class/spr2012/code/ocean_carbon.f
Orbital Configurations

If a molecule is **oxidized**: it has lost an electron
- O: greedy for electrons

If a molecule is **reduced**: it has *gained* an electron
- H: eager to give away its lone electron