Exam #2: Friday, 3/8

- All students will take the exam in Rm 228 Natural History Building
- If you must miss this exam, please send me an e-mail explaining the conflict (shurst@uiuc.edu)
- Material: Classes 11 through 20
- Q and A session: Thurs., Mar. 7th, 5-6 PM here (213 Greg)

Lecture 18 -- The Oceans

More on the chemistry of the Oceans...

DISSOLVED GASES IN SEA WATER

- **Solubility of atmospheric gases**
- **CO_2 and O_2 -- Role of biological processes**
- **The dissolved "CO_2"system in sea water**
  - **... "buffers" against sudden chemical changes**
  - **... controls $CaCO_3$ saturation**

ATMOSPHERIC GASES

- **Composition of atmosphere**
- **Atmospheric gases in sea water**
- **saturation ~ equilibrium**

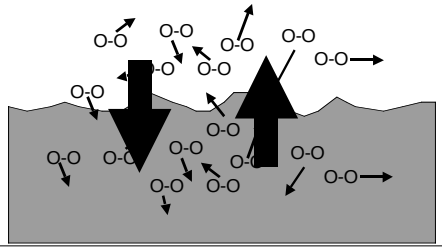
	Percent in atmosphere	Equilibrium concentration in seawater (ppm, or mg/kg)
N_2	78%	12.5
O_2	21%	7
Ar	1%	0.4
CO_2	0.03%	90 ← Why?

Chemical Equilibrium

Equilibrium- State of balance between opposing processes

Example: O_2 dissolved in seawater, in contact with air

- Constant vibration of all molecules
- Some O_2's in air colliding with water surface
- Some O_2's breaking free of the surface



Equilibrium concentration depends on ...

- **Temperature -- colder sea water holds more dissolved gas**
- **Salinity -- low-S sea water holds more gas**
- **Pressure -- sea water at depth holds more gas than shallow water**

High solubility of CO_2 -- Why???
It reacts with water to form anions.

Chemical reactions:

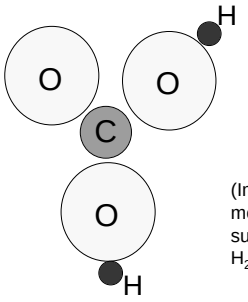
$$CO_2(g) \leftrightarrow CO_2(d)$$

$$CO_2(d) + H_2O \leftrightarrow H_2CO_3 \quad \text{[carbonic acid]}$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad \text{[bicarbonate]}$$

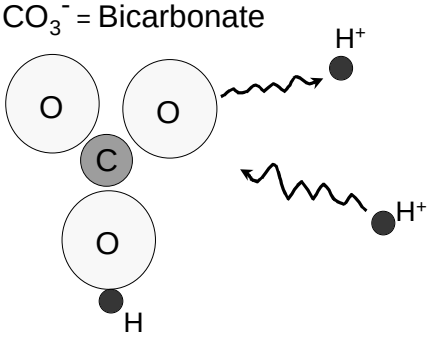
$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad \text{[carbonate]}$$

H_2CO_3: Carbonic Acid

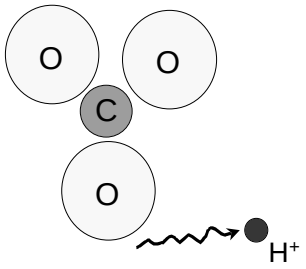


(Imagine this molecule surrounded by H_2O molecules)

HCO_3^- = Bicarbonate



CO_3^{2-} Carbonate



These reactions usually proceed until equilibrium is established.

$$CO_2(g) \leftrightarrow CO_2(d)$$

$$CO_2(d) + H_2O \leftrightarrow H_2CO_3 \quad \text{[carbonic acid]}$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad \text{[bicarbonate]}$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad \text{[carbonate]}$$

"Total Dissolved Carbon" in sea water (TDC) = sum of all species

$CO_2(d) + H_2CO_3$	1 %
HCO_3^-	93 %
CO_3^{2-}	6 %

DISTRIBUTION OF CO_2 AND O_2 -- ROLE OF BIOLOGICAL PROCESSES

Photosynthesis (Ph) and Respiration (Re)

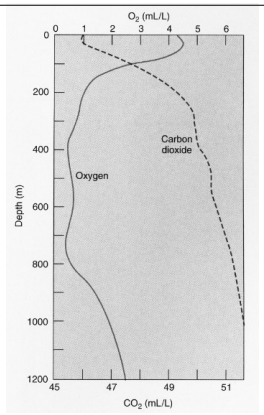
$$CO_2 + H_2O \underset{\text{Re}}{\overset{\text{Ph}}{\rightleftharpoons}} \text{"}CH_2O\text{"} + O_2$$

Total Ph rate ~ Total Re rate for oceans, overall
But in any one place, Ph ≠ Re

O_2 and CO_2 Concentrations Depend on Ph vs. Re Balance

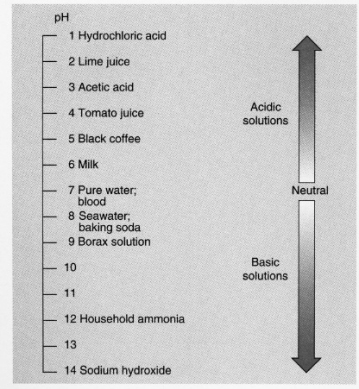
- Ph occurs only in upper 150 m ("photic zone")
  - Ph > Re, so $[O_2]$ is high
  - $[CO_2]$ is controlled by equilib. w/ atmosphere
- Re continues strongly at 200-800 m (Ph = 0)
  - $[O_2]$ is low ("oxygen minimum zone")
  - $[CO_2]$ is high, greater than at surface
- Re continues weakly at depth -- but $[O_2]$ increases!
  - Convection currents toward the bottom
  - Cold, O_2-saturated water sinking at high latitudes and spreading at depth.

Fig. 5.17



What is pH?

- **$[H^+]$ = concentration of H^+ (very important)**
- **It varies over a huge range:**
  - **Coca Cola: $[H^+] = 0.01$, or 10^{-2}**
  - **Ammonia: $[H^+] = 0.000000000001$, or 10^{-12}**
- **Better to just use the exponents....**
- **Define pH: - log $[H^+]$**
  - **Coca Cola: $[H^+] = 10^{-2}$, pH=2**
  - **Ammonia: $[H^+] = 10^{-12}$, pH=12**



DISSOLVED CO_2 SYSTEM:
Buffers the pH, i.e., resists changes in acidity

- Life processes and many chemical reactions sensitive to pH
- Reactions between "CO_2" species consume (or produce) H^+

$$CO_2(g)$$
$$\text{----}\uparrow\downarrow\text{---}$$
$$CO_2(d) + H_2O \leftrightarrow H_2CO_3$$
$$\uparrow\downarrow$$
$$H^+ + HCO_3^-$$
$$\uparrow\downarrow$$
$$H^+ + CO_3^{2-}$$

Example:

Catastrophic release of acid (H^+) to oceans (e.g., gigantic volcanic eruption)

CO_3^{2-} converts to HCO_3^-
Absorbs acidity
Avoids major change in $[H^+]$

2. "Buffers" the earth against big changes in atmospheric CO2 content.

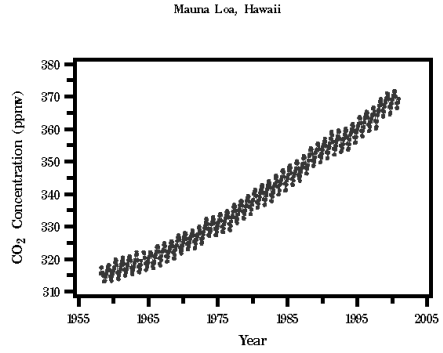
$CO_2(g)$
$\text{----}\uparrow\downarrow\text{---}$
$CO_2(d) + H_2O \leftrightarrow H_2CO_3$
$\uparrow\downarrow$
$H^+ + HCO_3^-$
$\uparrow\downarrow$
$H^+ + CO_3^{2-}$

$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$

Response of ocean to increased atm. CO_2

- Some of CO_2 enters ocean --> increases $[H^+]$
- Solid $CaCO_3$ dissolves -- consumes (neutralizes) H^+
- More CO_2 can dissolve (~50% of CO_2 produced by human activity has dissolved in oceans).

year	atm. CO_2	
1850	280 ppm	
		Fossil-fuel burning
		Deforestation
1998	360 ppm	



http://cdiac.esd.ornl.gov/trends/co2/sio-mlo.htm

3. Respiration in deep ocean controls $CaCO_3$ saturation (CCD)

- Respiration releases CO_2 --> increases $[H^+]$
- $CaCO_3$ is not stable in deep waters with this extra acidity-- it dissolves

Chemical Transformations Dissolved "CO_2" System

$CO_2(g)$
$\text{----}\uparrow\downarrow\text{---}$
$CO_2(d) + H_2O \leftrightarrow H_2CO_3$
$\uparrow\downarrow$
$H^+ + HCO_3^-$
$\uparrow\downarrow$
$H^+ + CO_3^{2-}$

$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$