Class 18

**DISSOLVED GASES AND**
**DISSOLVED INORGANIC CARBON IN SEA WATER**
**Chemical Equilibrium**
**Solubility of atmospheric gases**
**$CO_2$ and $O_2$ -- Role of biological processes**
**The dissolved inorganic carbon (DIC) system in sea water**
**..."buffers" against sudden chemical changes**
**... controls $CaCO_3$ saturation**

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**GASES IN THE ATMOSPHERE and the amounts of them dissolved in ocean water:**

| Molecule | Percent in atmosphere | Equilibrium concentration in seawater (mg/kg) |
|---|---|---|
| $N_2$ | 78% | 12.5 |
| $O_2$ | 21% | 7 |
| Ar | 1% | 0.4 |
| $CO_2$ | 0.03% | 90* |

*Note: This includes all four forms of $CO_2$

**Why is $CO_2$ so abundant in seawater when it is not very abundant in the atmosphere?**
**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 and entering water
Some $O_2$'s breaking free of the surface

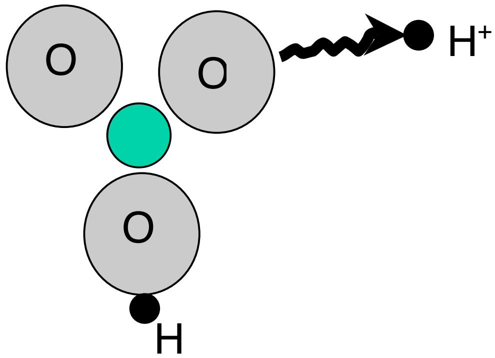
If the conditions stay the same, eventually the system stops changing, because these two opposing processes eventually balance each other.
That is equilibrium.

If the system has reached equilibrium then we can calculate the amount dissolved from simple equations. If it is not at equilibrium, the system will change over time and predicting its state is much more difficult.

**At the ocean's surface, gases are in equilibrium between water and atmosphere**
**Saturated = at equilibrium**
**Solubility = concentration at equilibrium**

**High solubility of $CO_2$ – Because it dissolves, reacts with water, and loses $H^+$ to form anions:**

$CO_2(g)$ **<=>** $CO_2(d)$
$CO_2(d) + H_2O$ **<=>** $H_2CO_3$ [carbonic acid]
$H_2CO_3$ **<=>** $H^+ + HCO_3^-$ [bicarbonate; an anion]
$HCO_3^-$ **<=>** $H+ + CO_3^{2-}$ [carbonate; an anion]




This diagram shows an $H^+$ ion splitting off from an $H_2CO_3$ molecule. This results in formation of an $HCO_3^-$ anion. Note: This grouping would be surrounded on all sides by water molecules.

Ions are much more stable (or favorable) as dissolved species than neutral molecules like $O_2$ and $N_2$, are.
Why? Because ions are attracted to and bonded with the + and - ends of the $H_2O$'s

**The various forms of DIC react quickly with each other and are always close to equilibrium in the oceans. Because of this, their percentage abundances are:**

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

**DIC SYSTEM -- IMPORTANT IN REGULATING SEA WATER AND ATMOSPHERE.**

1. **It "buffers" changes in acidity** (= concentration of H+)
   Note: pH = - log [H+], just a convenient notation, saves time
   Life processes and many chemical reactions are sensitive to pH
   Reactions between DIC species consume (or produce) H+
   These reactions are fast and equilibrium is maintained
   **Example: Catastrophic release of H+ to oceans**
      (e.g., huge volcanic eruption)
   Higher $H^+$ conc. means more collisions of H+ with $HCO_3^-$ and $CO_3^{2-}$
      $H_2CO_3 <=> H^+ + HCO_3^-$
      $HCO_3^- <=> H+ + CO_3^{2-}$
   Drives the three reactions above to the left. In other words, the excess $H^+$ is quickly consumed because it bonds with $CO_3^{2-}$ or $HCO_3^-$
   $H^+$ concentration is held at an almost constant values because it is constrained by the equilibria between the DIC species.

**2. It "buffers" ocean-atm. system against big changes in atmospheric $CO_2$ content.**

Changes in atmospheric $CO_2$ conc.:

in 1850, $CO_2$ conc. = 280 ppm

…but then Fossil-fuel burning, Deforestation added $CO_2$

in 1998, $CO_2$ conc. = 360 ppm

Response of ocean to increased atm. $CO_2$:

Some of this $CO_2$ dissolves into oceans

Converts to $HCO_3^-$ and $CO_3^{2-}$, stays dissolved

estimate: ~50% of CO2 produced by human activity has dissolved into oceans.

3. **Atmospheric CO2 content has gotten so high the added carbonic acid has changed pH a little**

This may start to impact coral reefs and certain key algae in the oceans

**$CO_2$ AND $O_2$ concentrations vary with depth**

-- depends on BIOLOGICAL PROCESSES

Photosynthesis (Ph) and Respiration (Re): Schematically....

Ph: $CO_2 + H_2O \Rightarrow CH_2O + O_2$

Re: $CH_2O + O_2 \Rightarrow CO_2 + H_2O$

Total Ph rate ~ Total Re rate for global oceans.

But, Ph rate vs. Re rate varies from surface waters to deep waters

**Therefore, DIC and [$O_2$] vary with depth...**

**Ph occurs only in top 150 m (sunlight needed)**

Ph > Re

[$O_2$] is high

DIC is controlled by equilibrium with air

**Re is dominant at 200-800 m (Ph = 0)**

$O_2$ is consumed, and therefore... [$O_2$] is low ("oxygen minimum zone")

DIC is high because $CO_2$ is produced

**Re continues at >800m, but slowly -- but [O2] increases, because...**

Cold, $O_2$-saturated water sinking at high latitudes and spreading at depth.

**Respiration in deeper layers of the ocean controls $CaCO_3$ saturation (CCD)**

Respiration releases $CO_2$

$CO_2$--> carbonic acid --> increases [H+]

$CaCO_3$ dissolves