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

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.

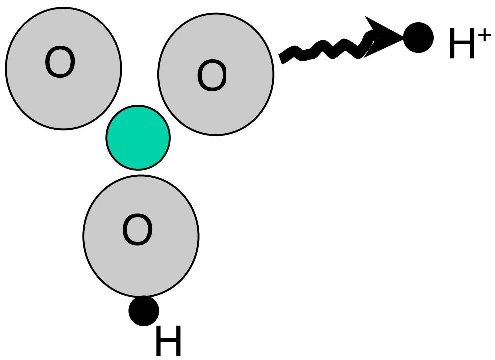
If the system has reached equilibrium then we can calculate the amount dissolved from simple equations. If it is not at equilibrium, the system will change over time and predicting its state is much more difficult.

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 %

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.

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-}
$H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$
$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$
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
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 in oceans.

3. 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