Physics and Chemistry of Sea Water

I. MATTER, ELEMENTS, ATOMS: BASIC CHEMISTRY REVIEW

A. Definitions

0. Matter- any material that occupies space and has mass.

1. Elements - all matter are made of elements, over 100 elements are known. Elements include O, Au, Ag, N, H, C and have a unique, and identifiable atomic structure.

   a. Refer to periodic table/handout
      (1) 92 naturally occurring elements
      (2) 11 man-made elements (103 total)

2. Compounds - combination of two or more elements joined together at the atomic level.

3. Atom - the smallest recognized particle of matter that retains the properties of a given element. Atoms of elements are combined together to form compounds.

B. Atomic Structure - Theory of atoms and atomic structure are based on experimental evidence and mathematical models. Atoms are generally too small to observe directly even with the most powerful microscope, but they can be observed indirectly by modeling.

1. Nucleus - central portion of an atom which contains even smaller sub-atomic particles called protons and neutrons.

   a. Protons - very dense, positively charged subatomic particles in the nucleus of an atom.

   b. Neutrons - dense, neutrally charged subatomic particles in the nucleus of an atom.

2. Electrons - negatively charged particles that orbit very rapidly about the nucleus of an atom. Generally considered that electrons are moving so fast, that it is difficult to locate their position at any given moment....view electrons as a cloud of charged particles hovering about the nucleus.

   a. Electron clouds are organized at certain distances from the nucleus in regions called energy level shells. Each energy level shell at a given distance from the nucleus can only hold a certain number of electrons at any given time. An important fact with regards to attraction and bonding together of atoms to form compounds...our concern since it relates to the construction of minerals and rocks.

3. Atomic number - is the number of protons located in the nucleus, each element has its own unique atomic number making it distinct from other elements (e.g. C a.n. = 6, O a.n. = 8)

b. Isotope: same number of protons, variable no. of neutrons

(1) e.g. O^{18}/O^{16}: 8 protons but 10 and 8 neutrons respectively

(2) Deuterium = hydrogen with proton + neutron: atomic no. = 2 (instead of one for common hydrogen with one proton)

(3) Tritium = hydrogen with 1 proton and 2 neutrons: atomic no. =3.

4. Atomic charge balance - all atoms contain the same number of negative electrons as positive protons, thus as neutrons have no charge, then net positive charges = net negative charges (protons = electrons)

Elements can be considered to be large collection of electrically neutral atoms, having the same atomic number or no. of protons.

5. Electron energy level shells - the lst principle shell holds 2 electrons, while each of the higher shells holds 8 or more electrons, but the outermost shell will contain a maximum of only eight electrons... an important phenomena in that the configuration of 8 electrons in the outermost shell tends to be a stable occurrence in nature.

C. Atomic Bonding - Chemical bonding between atoms occur when two or more elements join to form a compound (e.g. Na and Cl atoms typically bond to form NaCl or table salt). The forces that bring atoms or ions (electrically charged atoms) together are electrical in nature and the configuration of the electrons in the outer energy shell are important in relation to bonding characteristics of a given element.

1. Octet Rule - atoms combine in order that each may attain an electron arrangement of eight in the outer energy level (the stable configuration that naturally occurs in Noble Gases).

a. Noble gases= stable/inert as outer shell filled with octet configuration

1) helium (2), neon (8), argon, xenon and radon.

In order to satisfy the octet rule, an atom can either gain, lose, or share electrons with one or more atoms. The electrons form an electrical glue which hold atoms together

2. Valence electrons - the electrons present in the outer energy level that are available for atomic bonding. The no. of valence electrons an element has determines the number of bonds it will form.

e.g. Si has 4 valence electrons and tends to form 4 bonds in the process of obtaining the stable configuration of 8 electrons in the outer energy level. Oxygen has 6 electrons in outer shel, and forms two bonds to complete to 8. Hydrogen has one electron in its first shell, thus only needs one bond to complete the stable configuration of 2 electrons in the first shell.

3. Ionic Bonds - bonding in which one or more valence electrons are transferred from one atom to another. One atoms becomes stable by giving up an electron (to obtain a stable no. in outer energy shell) the other atom becomes stable by accepting one electron into its outer energy shell. The result is oppositely charged ions attracting to one another to produce an electrically neutral stable compound.

e.g. NaCl - Na has an atomic no. of 11, and thus contains 11 electrons around the nucleus (2 in first energy level, 8 in second energy level, and 1 in valence or outer energy level); Cl has an atomic no. of 17 and thus 17 electrons about its nucleus (2 in first level, 8 in second level, 7 in outer level). Thus Na needs to lose 1 electron from outer shell to obtain stable configuration, and Cl needs to gain 1 electron in outer shell to obtain stable configuration.... tendancy for ionic bonding to form NaCl.

a. Ions - electrically charged atoms.

1) positive ions (CATIONS) - tend to lose electrons during bonding (e.g. Na in its native state has an atomic no. of 11, thus 11 positive protons in nucleus, and 11 negative electrons about the nucleus making it electrically neutral. When it loses one electron during bonding it then has 11 positive protons and 10 negative electrons and thus has a net +1 positive charge.

2) negative ions (ANIONS) - tend to gain electrons during bonding. Cl on the other hand has an atomic no. of 17 with 17 +protons and 17-electrons in its native state, it tends to gain 1 electron during bonding thus results in 17+protons and 18 - electrons and a net charge imbalance of -1. Na +1 and Cl -1 attract one another as they have opposite and equal charges.

Thus two elements with different properties combine together to form a compound with yet different properties. Cl is a green poisonous gas, Na is a silvery reactive metal, but together they form NaCl or table salt also known as the mineral Halite.

4. Covalent Bonds - not all atoms combine by transferring/losing electrons to form ions. It is more beneficial in some cases for atoms to share valence electrons as opposed to transferring them to obtain a stable configuration.

Covalent Bonds - bond produced by sharing of electrons to obtain stable arrangement of 8 electrons in outer energy shell

e.g. Cl_2 or chlorine gas - occurs as 2 atoms of chlorine share their outer electrons ... see page 21....as stated previously, Cl has 7 electrons in its outer shell, thus if it lossed any electrons it would become more unstable, so in the case of two cl atoms they simply share their to valence shell electrons

a. Metallic bonding - extreme case of electron sharing in which electrons move freely from atom to atom. Metallic bonding accounts fo the high electrical conductivity of metals and other special properties.

II. **Physical Properties of Water**

A. Can exist in all three physical states: liquid, solid (ice), and gas (water vapor)

B. Transformation Processes related to energy input and entropy of water: heating of water, > atomic activity of the water molecules, i.e. > vibrational energy of water atoms.

   1. ICE ----------HEAT----- WATER-------HEAT -------WATER VAPOR
      (<32 degrees) (32-212) (>212 degrees F)

C. Water is one of few earth substances that remains in a liquid state at the operating surface temperatures of the earth.

   1. The liquidity of water makes it a dominant and pervasive component of all earth processes

D. Water has High Heat Capacity- it has a capacity to absorb and hold energy with only a small amount of temperature rise.

   1. important for water-based organisms to regulate temperature
   2. produces the moderating effects of oceans on climate
      a. oceans = warm residual heat in winter (warms air temp.)
      b. oceans = slow rate of heating in summer (cools air temp.)

E. Water expands in volume when it freezes/ becomes colder, in contrast to majority of substances (which contract when colder)

   1. Result Density of ice < Density of water: thus ice floats on water

F. Water strongly influenced by the force of gravity, constantly driven downward, and can possess great erosive/ landscape carving force

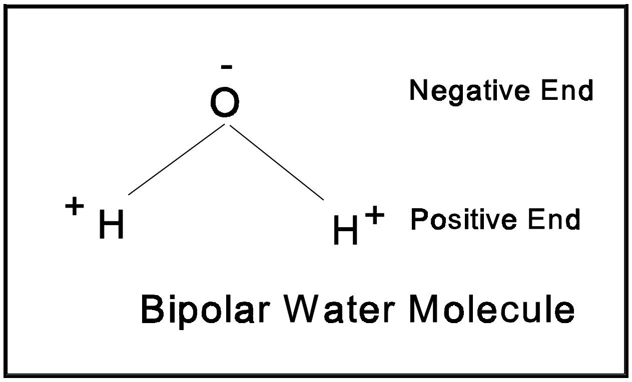
G. Water has property of high surface tension, ability to have strong molecular attractive forces (sticks to itself and electrostatically attracts ionic forms of elements)

   1. Capillarity- phenomena of water moving upward against the force of gravity, due to strong electrostatic adhesive forces, most notable in narrow, restricted pore spaces where surface to surface contact in high.

H. Water acts as a "universal solvent" and can dissolve most any substance over time. Water + carbon dioxide forms a mild carbonic acid solution naturally in hydrosphere, as an acid can result in cationic exchange with positive ionic species, and result in chemical breakdown of substances.

   1. Bipolar Water Molecule H_2O
   2. Covalent bonds between hydrogen and oxygen (strong bond, via sharing of electrons)

a. Hydrogen: 1 valence electron (atomic no. of 1)
b. Oxygen: 6 valence electrons (atomic no. of 8)



3. Hydrogen bonds- given a mass of water molecules, the opposite ends will attract molecularly, forming hydrogen bonds
   a. hydrogen bond between molecules is weaker than covalent within molecules
      (1) water mass is fluid, but molecules are difficult to dissociate

I. Light Penetration of Water

1. Light = portion of electromagnetic spectrum

   a. EM spectrum classified by wavelength and frequency
      (1) visible light: wavelength range: 0.01 to 1000 micrometers
      (2) short wavelengths = blue end of spectrum
      (3) long wavelengths = red end of spectrum

2. Incoming solar radiation on oceans
   a. energy reflection
      (1) bounce off the surface of ocean
      (2) albedo - measure of reflectivity of earth surface
   b. energy refraction
      (1) penetrate and bend as light passes through water
      (2) air-water interface = velocity change
   c. energy absorption
      (1) absorption of energy / photosynthetic energy

3. Light Absorption and Ocean Water

Depth (m)	% Absorption	% Transmittance
1 m	55%	45%
10 m	84%	16%
100 m	99%	1%

   a. Absorption according to selective wavelengths
      (1) red end absorbed first at shallow depths
      (2) blue-green end absorbed at greater depths

b. Factors affecting visibility
   (1) water chemistry
   (2) turbidity - concentration of suspended sediment

4. Sound Transmission in Seawater

   a. average velocity = 1450 m/sec (air = 334 m/sec)
   b. sound vel > with > temperature, > salinity, >pressure

Overview of Physical Properties of Water

A. Temperature-Density-Viscosity Relations

Temp. (C)	Density (gm/cm3)	Viscosity (centipoises)
5	0.999965	1.5188
10	0.997000	1.3097
15	0.999099	1.1447
20	0.998203	1.0087
25	0.997044	0.8949
30	0.995646	0.8004
35	0.99403	0.7208
100	0.95865	

B. Weight Density of Water

at 40 F, weight density = 62.4 lb/ft^3 (1 ft^3 = 7.48 gallons)
at 200 F, weight density = 60.135 lb/ft^3

C. Boiling Points of Water vs. Elevation (atmospheric pressure)

Elevation (ft)	Boiling Point (F)
-1000	213.8
0	121
5000	202.9
10,000	193.7

IN-CLASS EXERCISE

How many pounds will 500 gallons of water weigh? Show all of your math work.

If someone were to give you 3000 pounds of water, how many gallons would you have? How many cubic feet? Show all of your math work.

III. Heat Energy and Thermodynamics (heat flow)

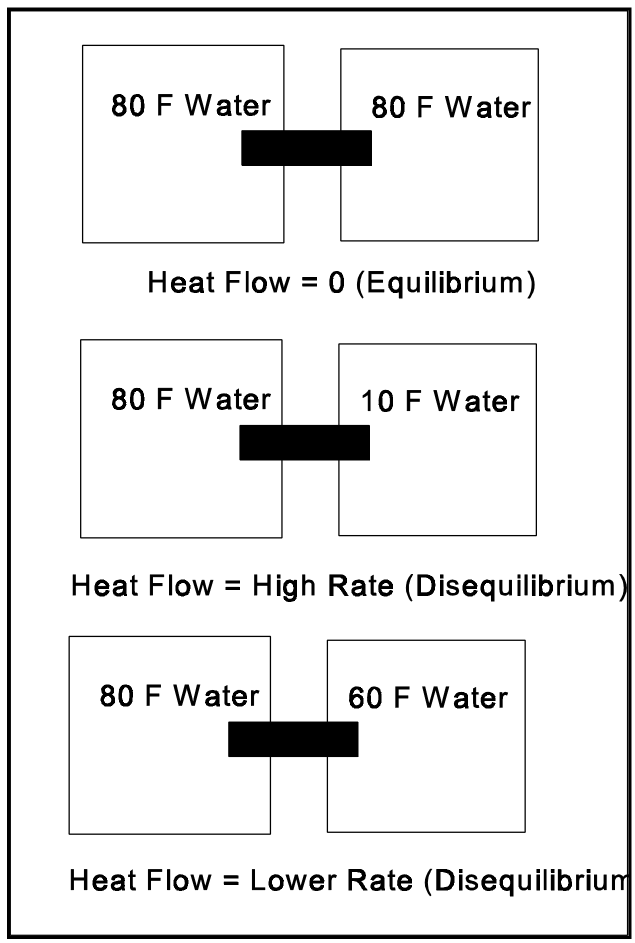
A. Heat - internal energy within a substance = kinetic molecular energy
   1. high heat substances = high degree of kinetic molecular energy
      a. i.e. the higher the heat the faster the vibration of atoms and molecules

   2. Temperature - measure of the average amount of heat energy in a substance - i.e. the average kinetic energy of a substance

B. Heat Flow
   1. "Thermodynamics" = study of heat, heat flow and behavior of heat
   2. Heat Flow : An Equilibrium Process
      a. Temperature Imbalance Causes Heat to Flow or Transfer
      b. Substances at Same Temperature = Temperature Equilibrium

   3. Heat Flows from High Temperature Regions to Low Temperature Regions
      a. At temperature equilibrium: net heat flow = 0
      b. The higher the temperature differential, the faster the heat flow
      c. The lower the temperature differential, the slower the heat flow

Consider an experiment with two vessels of water, with variable heat-content. They are connected by a tube that allows heat to exchange between the two vessels.



      d. Specific Heat Capacity
         (1) Amount of heat required to raise the temperature of 1 gram of a

substance, 1 degree C

(2) E.g. Water has high heat capacity compared to rock

(a) takes a higher amount of heat to raise the temperature of water, compared to rock

(b) Result: water heats and cools more slowly than earth /rocks

C. Heat, Expansion, Contraction

1. Expansion of Hot Matter

a. Increase heat, increase temperature, increase vibrational kinetic energy of atoms / molecules

(1) atoms/molecules vibrate faster - move farther apart to make room

(2) Net Result: Expansion and Volume Increase

2. Contraction of Cold Matter

a. Opposite Relation: remove heat, < temperature ... volume decrease / contraction

3. Density Relations to Heat-Induced Volume Changes

a. Density = mass / volume

(1) assuming mass is constant, when volume decreases, density increases

(2) assuming mass is constant, when volume increases, density decreases

(a) i.e. an "inverse relationship" between density and volume

b. Heat Loss = Cooling = < kinetic energy = < volume = > density

c. Heat gain = Warming = >kinetic energy = > volume = < density

(1) e.g. Hot Air Balloon: Hot Air = volume increase = density decrease

(a) less dense hot air rises relative to more dense cold air

4. States of Matter vs. Volume Change / Density Change

a. Solids = decreased temperature = decreased kinetic energy = decreased volume = increased density

b. Gases = increased kinetic energy = increased volume = decreased density

5. Special Consideration: Water

a. Most substances are more dense in a solid state compared to a liquid state

b. Water is the opposite

(1) Density of Ice (solid water) = 0.92 gm/cm^3

(2) Density of Water (liquid) = ~1.0 gm/cm^3

(a) Result: Ice Floats in Water

(3) Why? Because the crystal structure of ice takes up more space (greater volume) than the structure of liquid water molecules

c. Importance: A good thing, otherwise oceans and lakes would freeze from the bottom - up... resulting in destruction of all aquatic life!!!

(1) Luckily: Lakes / oceans freeze with ice on the surface, and liquid water insulated from freezing at depth.

D. Heat Transfer

1. Mechanisms of Heat Transfer

a. Conduction: heat and vibrational kinetic energy is passed from molecule to molecule, without actual transfer of mass
(1) heat transfer without mass transfer
(2) e.g. heating an iron rod, the heat is transferred from one end to the other without transfer of mass
(3) Examples
(a) Good conductors of heat = iron / metal (rapidly transmit heat)
(b) Poor conductors of heat = adobe / brick, fiber glass insulation
(c) Poor conductor = "good insulator"

b. Convection - heat transferred via transfer of mass
(1) e.g. "fluid currents" transfer heat
(2) Convection cells common in ocean, atmosphere, and earth's interior
(a) e.g. Warm air rises, cools, sinks
(b) e.g. Warm ocean water rises, cools, sinks

c. Radiation - heat transfer via electromagnetic radiation
(1) infrared radiation = "thermal radiation"
(2) remember: infrared = wavelengths longer than visible spectrum

(3) Emitters of radiant energy
(a) Sun (hydrogen fusion)
(b) Earth (radioactive decay of elements)

E. Temperature, Energy and Influence on Physical State

1. Three physical states of matter (water in this case) - dependent on amount of heat energy (vibrational kinetic energy) contained within matter
a. solid (low energy)
(1) crystalline atomic structure
b. liquid (medium energy)
(1) fluid - material changes shape easily
c. gas (high energy)
(1) fluid - material changes shape easily

2. Transformation Processes related to energy input and entropy of water: heating

of water, > atomic activity of the water molecules, i.e. > vibrational energy of water atoms.

ICE ----------HEAT----- WATER-------HEAT -------WATER VAPOR
(<32 degrees) (32-212) (>212 degrees F)

3. Evaporation- process of transforming water from liquid to gaseous state (Heat Gain)

4. Freezing- process of transforming water from liquid to solid state (Heat Loss)

5. Condensation- transformation of water vapor to liquid form (Heat Loss)

6. Sublimation- process of transforming ice to water vapor directly through superheating, bypassing liquid form. (Heat Gain)

F. Thermal Budget and States
   1. States of matter a function of amount of heat in system, which in turn influences the vibrational rates of molecules
      a. gas - high rate of vibration, high heat condition
      b. liquid- medium rate of vibration, medium heat system
      c. solid- low rate of vibration, low heat system

   2. Heat Energy
      a. measured in calories
         (1) amount of energy required to raise the temperature of 1 gram of water 1 degree C

   3. Heat and State Transformation
      a. Evaporation: water liquid to vapor = system must absorb 600 Cal of energy
         (1) energy absorbed by molecules, > rate of vibration to allow phase change

         (2) latent heat of vaporization = "stored heat" that is exchanged to cause phase change

      b. Condensation: water vapor to liquid = system must lose 600 Cal of energy
         (1) < vibratory motion
         (2) latent heat of condensation
         (3) Condensation/heat transfer
            (a) drives storm systems
            (b) affects climate
            (c) transfers heat from equator to poles
            (d) results in cloud phenomena

      c. Melting: solid ice changed to liquid = system must gain 80 calories of energy

d. Freezing: liquid to solid = system must lose 80 calories of energy
  (1) latent heat of fusion for water

e. Sublimation: solid to gas or gas to solid = system must gain 680 cal of energy or lose 680 cal of energy respectively for transformation to occur
  (1) e.g. dry ice sublimates to gaseous carbon dioxide with no intervening liquid phase

G. Basic Laws of Classical Physics

1. Conservation of Mass - mass is neither created nor destroyed
2. Conservation of Energy - energy is neither created nor destroyed
3. Newton's Second Law of Motion: F = ma (force is equal to mass x acceleration)

IV. pH and the Calcium Carbonate System as Related to Sea Water

Calcium Carbonate System

a. <u>pH Defined</u>

(1) pH Defined: the "activity" of hydrogen ions in a solution; defines the concepts of acidity and alkalinity.

(a) "activity" = essentially equivalent to the effective concentration of a given ion in solution.

(b) By definition, a pure substance such as water, or a solid mineral, has an activity = 1.0.

(c) The lower the overall concentration of ions in solution, the closer activity= concentration.
  i) As concentration of dissolved ions increases, e.g. seawater, activity of a given ion is generally < than its conentration.

  ii) activity accounts for resistive interference of given ions to reaction, by other electrostatically charged ions in solution.

(d) Hence pH = negative log base 10 of hydrogen ion activity of a solution:

$pH = -\log_{10}[H+]$

H activity = 0.0001 = 10^{-4} pH = $-\text{Log}_{10}(10^{-4})$ = 4 (acidic)
H activity = 10^{-14} pH = $-\text{Log}_{10}(10^{-14})$ = 14 (basic)

1. <u>Calcium Carbonate Stability as Function of pH</u>

a. Definitions:

(1) Ion Solubility: the relative ability of ionic/elemental species to dissolve into solution. High Solubility = very dissolvable

(2) Mineral Precipitation: the crystallization of solid compounds from ionic species in a solution.

(3) Solution Equilibria

(a) "Saturated" Solution: a condition in which the rate of precipitation = rate of dissolution for a given set of ionic species.

(b) "Undersaturated" Solution: a condition in which a solid mineral species or compound will readily dissolve into solution, if soluble.

(c) "Supersaturated" Solution: a condition in which a ionic species will readily combine to precipitate out of solution.

2. Important reactions involving CO_2, H_2O, $CaCO_3$, and pH.

a. Dissolution of Carbon Dioxide (gas) in water results in production of Carbonic Acid, which subsequently dissociates into free H^+ ions and the bicarbonate anion

(HCO_3^-), hence increasing hydrogen ion activity, and by definition decreasing pH (becoming more acidic).

$CO_2 + H_2O$ ------ H_2CO_3

H_2CO_3 ------- H+ + HCO_3-

$CO_2 + H_2O$ ---- H+ + HCO_3-

b. As Calcium Carbonate (solid) reacts with water in presence of free hydrogen ions, the solid Calcium Carbonate dissolves forming free Ca^{+2} ions and free bicarbonate ions, hence consuming free hydrogen ions, decreasing hydrogen ion activity, and by definition increasing pH (becoming more basic). i.e. Calcium Carbonate acts to neutralize or buffer the solution by consuming hydrogen ions.

$CaCO_3 + H_2O + CO_2$ ------ Ca_{+2} + $2HCO_3$-

c. Dissolution of Calcium Carbonate as a Function of pH

d. General relationship: as Carbon Dioxide content of water increases, hydrogen ion actvity increases, pH decreases (more acidic)------solid

Calcium Carbonate undergoes dissolution

(1) Dissolved Carbon Dioxide content is temperature dependent, as T >, Carbon Dioxide content <, hence hydrogen ion activity decreases, pH increases (conducive to calcium carbonate precipitation)

As T <, Carbon Dioxide content >, hence hydrogen ion activity increases, pH decreases (conducive to calcium carbonate dissolution)

Hence >T, <P, <CO2, >pH, Calcium Carbonate Precipitation
<T, >P, >CO2, <pH, Calcium Carbonated Dissolution

e. In Sum: carbon dioxide in water creates carbonic acid and limestone dissolves

(1) If carbon dioxide is decreased pH > and calcite precipitates

V. Composition of Seawater

A. Ionic components

Ion	% by wt.	g/1000 g (ppt)
Na	30.66	10.77
Mg	3.65	1.29
Ca	1.17	0.41
K	1.13	0.40
Sr	0.023	0.008
Cl	55.2	19.35
SO_4	7.71	2.71
HCO_3	0.3	0.12
Br	0.19	0.067

B. Total Constituents in 1 kg of average sea water

	mass (g)
H_20	965.31
Cl^-	19.10
Na^+	10.62
SO_4^{-2}	2.66
Mg^{+2}	1.28
Ca^{+2}	0.40
K^+	0.38
all others	0.25

C. Other Chemical Properties

1. Salinity -measured of dissolved ions in sea water
   a. units = parts per thousand = ppt = g of solute / kg of water
   b. Empirical relationship: Salinity (ppt) = 1.81 x (conc. Cl^- in ppt)
   c. Source of dissolved solids in ocean
      (1) chemical weathering of continental and oceanic crust
      (2) volcanic eruptions (seafloor vents)
      (3) river transport of dissolved load
   d. salt cycle
      (1) evaporite formation vs. weathering/dissolution

2. Controlling Factors of Density
   a. temperature (> temp, < density)
   b. salinity (>salinity, > density)
   c. Density-temperature stratification of water bodies

3. Vertical Structure of Oceans (Latitude Controlled: solar influx)
   a. Pycnocline = density gradient with depth
   b. Thermocline = temp. gradient with depth
   c. Halocline = salinity gradient with depth

4. Carbon Dioxide Solubility
   a. carbon dioxide highly soluble in sea water (see above)

5. Alkalinity / Buffering Capacity
   a. alkalinity - measure of ability to consume free H+ ions
      (1) source of alkalinity in oceans
         (a) $HC0_3^-$ (bicarbonate anions)
         (b) CO_3^{-2} (carbonate anions)
         (c) dissolution of CaCO3 from seafloor, consumes H+ ions
   b. buffering capacity = alkalinity is a measure of solution's ability to consume H+ ions, and maintain constant pH