CEE 543: WATER CHEMISTRY

COURSE LOGISTICS

- MWThF 8:30 MORE 225
- TEXT and REFERENCES
- WEBSITE: http://faculty.washington.edu/markbenj/CEE543
  - Links to HW assignments, solutions, errata, etc.
- Grading: HW, Midterm, Final exam, Participation
- Expectations
  - Attend class
  - Read assignments in advance
  - HW (best to work together)

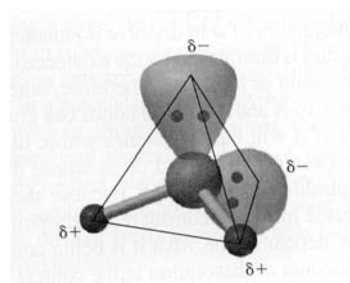
- **Chemical equilibrium**
- **Size and shape of water molecules; space between molecules**
- **Conc'n of water in environmental solutions**
- **Polarity**
- **Hydrogen bonds**
- **Dissolution**
- **Dissociation**
- **Salts, ions**
- **Hydrophobic/hydrophilic**
- **Conc'n of solutes in environmental solutions**
- **Units for expressing conc'n – mol/L, ppm, ppb, equiv/L**
- **pX**
- **Ionic strength, conductivity, TDS, hardness**
- **Chemical (re)activity**

Course Overview

- Focus on quantitative description of the ***equilibrium composition*** of an aqueous solution: what it is in a given system; what we have to do to alter it in a desired way
  - **Equilibrium**: No net production or destruction of chemicals via a specified chemical reaction (same concept can be applied collectively to all reactions in a given system)
  - **Composition**: Emphasis is on ***speciation*** of key components, meaning the distribution of the components among different chemical forms
    - e.g.: H_2S vs. SO_4^{2-}; NH_4^+ vs. NH_3; Cr^{3+} vs. CrO_4^{2-}; HOCl vs. Cl^-
- Composition of systems of interest
  - Overwhelmingly H_2O (55.5 mol/L as a pure liquid); other constituents comprise $<10^{-9}$ to a few percent of all molecules in solution
  - Key water quality issues and regulations cover a similar range (e.g., THMs, EDCs; metals; hardness)

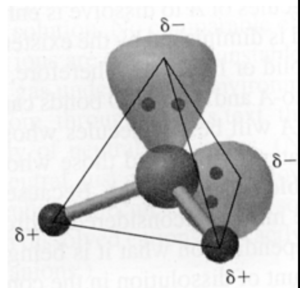
Water: Molecular Structure and Key Properties

- Molecular size
  - Single H_2O molecule has ~1 Å (0.1 nm) equivalent diameter
  - Liquid water contains 1 molecule H_2O per ~30 Å^3, corresponding to occupation of a space with an equivalent diameter of ~4 Å



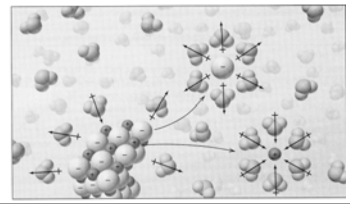
Water: Molecular Structure and Key Properties

- Oxygen-centered tetrahedron, with H^+ ions (bare protons) at two corners and unshared electron pairs at other two corners
  - ***Dipolar***, facilitating interactions with other dipoles or charged molecules (ions)
  - Structure facilitates formation of ***hydrogen bonds***, leading to unusually high density and cohesiveness (high boiling point, surface tension)
  - Up to four H bonds can form; three typically exist at normal temperatures



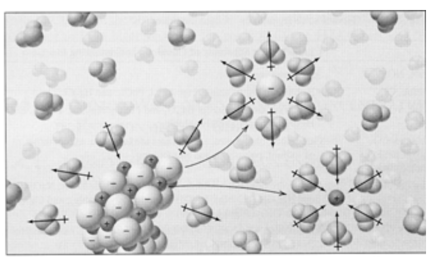
Jargon for Characterizing Water/Solute Interactions

- Dissolution: Surrounding of individual molecules of solute by water molecules
  - Requires breaking of H bonds in solution and solute-solute bonds in the undissolved molecules, both of which oppose dissolution
  - Formation of bonds between H_2O and solute favors dissolution
  - Above competition plus randomizing effect of molecular kinetic energy controls dissolution; designation of a compound as "hydrophobic" or "hydrophilic" is always relative to some implicit baseline



Jargon for Characterizing Water/Solute Interactions

- Some compounds ***dissociate*** (i.e., split apart) when they dissolve
  - Compounds that dissociate extensively and release ***ions*** in the process are called ***salts***
  - Positive ions are ***cations***; negative ions are ***anions***; all ions are hydrophilic



Expressing Solute Concentrations

- Dimensions and Units
  - Mass/volume (e.g., mg/L, mg/m^3, mol/L [molar, *M*; really, #/L])
  - Mass/mass (e.g., mg/kg, mass fraction, ppm_m, ppb_m, mol/kg [molal, *m*; really, #/kg])
  - Mol/mol (mole fraction)
  - Volume/volume (e.g., volume fraction, ppm_V); used primarily for gases
- The "*p*-convention": $pX \equiv -\log_{10}(X)$, where *X* is a value that must be understood from context. Most often, *X* is a molar concentration, a chemical activity (a concentration-like term to be defined shortly), or a product of such terms.
- Composite or Surrogate Concentrations
  - Used to characterize mixtures of species that behave similarly or when the individual species are unknown
  - Examples: Total or Dissolved Organic Carbon (TOC or DOC), Alkalinity (Alk), Total Organic Halogen (TOX), Hardness (Hd^{2+}); Free Available Chlorine (FAC); Ammonia-N (NH_3-N)

Expressing Solute Concentrations

- Concentrations Expressed As an Equivalent Amount of a Different Species or Other Item
  - Often used to express concentrations of chemical composites
  - Species used for "equivalency" is usually logical, but sometimes obscure (based on a historical convention that is no longer relevant; e.g., hardness *as* $CaCO_3$)
  - Basis of the equivalency is usually implicit and therefore potentially ambiguous (10 pennies are equivalent to one dime in terms of purchasing power, but not in size, mass, etc.)
- Examples
  - Charge (one mole of Ca^{2+} is two equivalents of charge)
  - Acquisition/release of H^+ in acid/base reactions: $H_2CO_3 \leftrightarrow 2H^+ + CO_3^{2-}$; one mole H_2CO_3 is two "acid equivalents"

- 10 μg/L Bromoform ($CHBr_3$, MW 250)

$$\frac{10\ \mu\text{g/L CHBr}_3}{1\ \mu\text{mol}/250\ \mu\text{g CHBr}_3} = 0.04\frac{\mu\text{mol}}{\text{L}}$$

$$0.04\frac{\mu\text{mol CHBr}_3}{\text{L}}\left(\frac{3\ \mu\text{mol X}}{\mu\text{mol CHBr}_3}\right) = 0.12\frac{\mu\text{mol TOX}}{\text{L}}$$

$$0.04\frac{\mu\text{mol CHBr}_3}{\text{L}}\left(\frac{[3\text{x}79.9]\ \mu\text{g Br}}{\mu\text{mol CHBr}_3}\right) = 9.48\frac{\mu\text{g Br}}{\text{L}}$$

$$0.12\frac{\mu\text{mol TOX}}{\text{L}}\left(\frac{35.5\ \mu\text{g Cl}}{\mu\text{mol X}}\right) = 4.26\frac{\mu\text{g TOX}}{\text{L}}\ \textit{as Cl}$$

Ionic Strength

- I or μ: A composite, calculated (not measurable) property of the solution (not of individual species)

$$I \equiv \frac{1}{2}\sum_{\textit{all ions}} c_i z_i^2$$

  - Always calculated using c values in mol/L, but commonly reported without dimensions
  - Includes contributions from all ions, but not neutral species
  - Indicator of the ability of the solution to neutralize the electrical field surrounding an ion (by attraction of like-charged and repulsion of oppositely-charged ions)
  - High ionic strength reduces an ion's "sphere of influence" and shields it from interactions with the rest of solution

Composite Parameters for Overall Solute Concentrations

- Conductivity, Specific Conductance (κ; microSiemens, μS)
  - Measurable indicator of overall ionic content of a solution
  - Includes contributions from all ions, weighted by their charge and mobility
- Total Dissolved Solids (TDS; mg/L)
  - Non-specific indicator of overall mineral content
  - Includes contributions from all solutes that do not easily volatilize (evaporate)