Basics of water quality
Water as a solvent

• Structure of water: dipole

- Highly polarized because of different electronegativity of O and H
- (-) charge on O, (+) charge on H

Dipole moment
A molecule has a dipole moment if the center of charge for the molecule’s positive charges is **NOT** at the same spot as the center of charge for the molecule’s negative charges

cf) O₂ – no dipole moment
Water as a solvent

Hydrogen fluoride

Dipole moment: 1.91 D

Water

Dipole moment: 1.84 D

Ammonia

Dipole moment: 1.30 D

Methane

Dipole moment: 0.0 D
Water as a solvent

• Hydrogen bonding

  - Weaker than covalent bond, but stronger than normal dipole-dipole interactions
  - Affect physical and chemical behavior of water in many ways
## Water as a solvent

<table>
<thead>
<tr>
<th>Property</th>
<th>H$_2$O</th>
<th>H$_2$S</th>
<th>CH$_4$</th>
<th>CH$_3$OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>18</td>
<td>34</td>
<td>16</td>
<td>32</td>
</tr>
<tr>
<td>Dipole moment (Debyes)</td>
<td>2.0</td>
<td>0.9</td>
<td>0.0</td>
<td>1.7</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>100</td>
<td>-60</td>
<td>-161</td>
<td>65</td>
</tr>
<tr>
<td>Enthalpy of vaporization (kJ/g)</td>
<td>2.30</td>
<td>0.55</td>
<td>0.88</td>
<td>1.10</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>0</td>
<td>-85</td>
<td>-181</td>
<td>-94</td>
</tr>
<tr>
<td>Enthalpy of fusion (kJ/g)</td>
<td>0.33</td>
<td>0.07</td>
<td>0.06</td>
<td>0.10</td>
</tr>
</tbody>
</table>
Water as a solvent

• High solubility for ions and polarized molecules
  ex) \( \text{Na}^+\text{Cl}^- \), \( \text{C}_2\text{H}_5\text{OH} \)

• Low solubility for non-polarized molecules
  ex) high molecular weight hydrocarbons

• Hydrophilic vs. hydrophobic

Tendency of water molecules to orient themselves around ions.

Water as a solvent

- Metals are often dissolved in the form of hydrated ions
- Examples
  - $\text{Na}(\text{H}_2\text{O})_4^+$
  - $\text{Ca}(\text{H}_2\text{O})_6^{2+}$
  - $\text{Fe}(\text{H}_2\text{O})_6^{3+}$
  - $\text{Al}(\text{H}_2\text{O})_6^{3+}$
Concentration units

- Molality (m)

\[ m, \text{mole/kg} = \frac{\text{moles of solute}}{1.0 \text{ kg of solvent}} \]

- Molarity (M)

\[ M, \text{mole/L} = \frac{\text{moles of solute}}{1.0 \text{ L of solution}} \]

- Mass concentration

\[ g/m^3 = \frac{\text{mass of solute, g}}{1.0 \text{ m}^3 \text{ of solution}} \]

1.0 g/m^3 = 1.0 mg/L

→ common mass concentration unit
Concentration units

• Normality \((N)\)

\[
N, eq/L = \frac{\text{equivalent of solute, eq}}{1.0 \text{ L of solution}}
\]

\((\text{meq/L more common})\)

* Equivalent mass

\[
\text{equivalent mass, g/eq} = \frac{\text{atomic (molecular)mass, g}}{z, eq}
\]

* Equivalent, \(eq = z \times \text{(moles of solute)}\)
  For acids, \(z\) is the number of replaceable hydrogen atoms; for oxidation-reduction reactions, \(z\) is the change in valence
**Concentration units**

- Parts per million (ppm)

\[
ppm = \frac{mass\ of\ solute, g}{10^6\ g\ of\ solution} = \frac{mass\ conc., g/m^3}{specific\ gravity\ of\ solution}
\]

*Also used are ppb & ppt for trace constituents*

- Mass concentration as CaCO₃
  - Traditional unit for alkalinity and hardness

  \[
  Note: \text{ meq mass of CaCO}_3 = 50 \text{ mg/meq}
  \]

  \[
  So, 1\ mM\ Ca^{2+}\ solution\ equals\ to\ what\ mg/L\ as\ CaCO_3?\n  \]

**Other \text{ \_\_ as \_\_}**

- Nitrogen: mg/L as N
- Phosphorus: % as P₂O₅
- Potassium: % as K₂O
Other useful chemical relationships

• Mole fraction
  – The ratio of the number of moles of a given solute to the total number of moles of all components in solution

\[ x_A = \frac{n_A}{n_A + n_B + n_C + \cdots n_N} \]

– For most aqueous solutions, the moles of water is so much larger than the moles of others, so the mole fraction can be approximated as:

\[ x_A \approx \frac{n_A}{55.6} \quad -- \text{why 55.6??} \]
Other useful chemical relationships

• Electroneutrality principle

\[ \sum \text{cations (in eq/L)} = \sum \text{anions (in eq/L)} \]

• Ionic strength

\[ I = \frac{1}{2} \sum_i (C_i \times z_i^2) \]

- Significance: in dilute solutions \((I \sim< 10^{-3} \text{ M})\) the ions behave independently of each other, but as ion concentration increases, ion interactions become significant, decreasing the activity of the ions
Other useful chemical relationships

- Activity and activity coefficients
  - {} vs. [ ]
    \[ \{i\} = \gamma_i[i] \]
  - \( \gamma_i \approx 1 \) in dilute solutions (for most natural waters except for seawater)
  - But otherwise \( \gamma_i \) can be significantly smaller than 1
  - Güntelberg equation (for \( I < 0.1 \)):
    \[
    \log \gamma_i = - \frac{0.5z_i^2 I^{0.5}}{1 + I^{0.5}}
    \]
Other useful chemical relationships

• Equilibrium constant
  – For reversible reactions

\[ aA + bB \rightleftharpoons cC + dD \]

\[ K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

– In dilute solutions

\[ K \approx \frac{[C]^c[D]^d}{[A]^a[B]^b} \]
Other useful chemical relationships

• Solubility product
  – Equilibrium constant for dissolution-precipitation reactions

ex) \[ CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \]

\[ K_{sp} = [Ca^{2+}][CO_3^{2-}] \]

⇒ \[ [Ca^{2+}][CO_3^{2-}] \] (dilute solutions)

\[ \text{For pure solids, activity} = 1 \]
Other useful chemical relationships

• Henry’s law
  – At relatively low concentration of gaseous compound in air, the concentration (or mole fraction) dissolved in water is proportional to the concentration (or partial pressure, mole fraction) in air
  – So, Henry’s law constant can have various different units
  – Unitless Henry’s law constant

\[ \frac{C_g}{C_s} = H_u \]

\( C_g = \text{concentration in gas phase (mg/L)} \)
\( C_s = \text{saturation concentration in liquid (mg/L)} \)
\( H_u = \text{unitless Henry’s law constant} \)
Water constituents

• Dissolved inorganics
  – Major in surface & ground water: Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^-\), HCO\(_3\)^-, SO\(_4\)^{2-}, SiO\(_2\) (mostly ionic)

• Dissolved organic matter (DOM)

• Suspended matter

• Microorganisms
  – attached/suspended
  – pathogenic/benign
Water constituents

- Organics in natural waters
  - Simple sugars, amino acids, etc.
    - Conc. typically very low – easily degraded
  - Microbial polymers
    - Extracellular components in biofilms, flocs, aggregates
    - In some cases may have significant dissolved concentrations
  - Humic substances
    - Typically the primary component of dissolved & particulate organic matter
      - Resistant to degradation
      - Molecular weights from ~500 to >100,0
      - Hydrophilic/hydrophobic regions
      - Coat minerals, photoactive, affinity to metals & organics
Water constituents

There’s no humic “molecule”!

http://www.euni.de
Water constituents

• Organics in natural waters - anthropogenic
  – >100,000 synthetic chemicals in daily use
    • Pesticides, solvents, dyes, personal care products, anti-fouling agents, additives
    • >300,000,000 tons produced annually
  – Widely varying properties
    • Size, aqueous solubility, volatility, degradability, toxicity
Water constituents

• **Suspended matter**
  - Operationally defined as the material that retained on a 0.45 μm filter
  - Colloids: 1 nm – 1 μm in size
  - Includes mineral colloids, microorganisms and their debris, organic polymers
  - Influences:
    • Contaminant transport
    • Light attenuation
    • Disinfection efficiency
    • Aquatic habitat