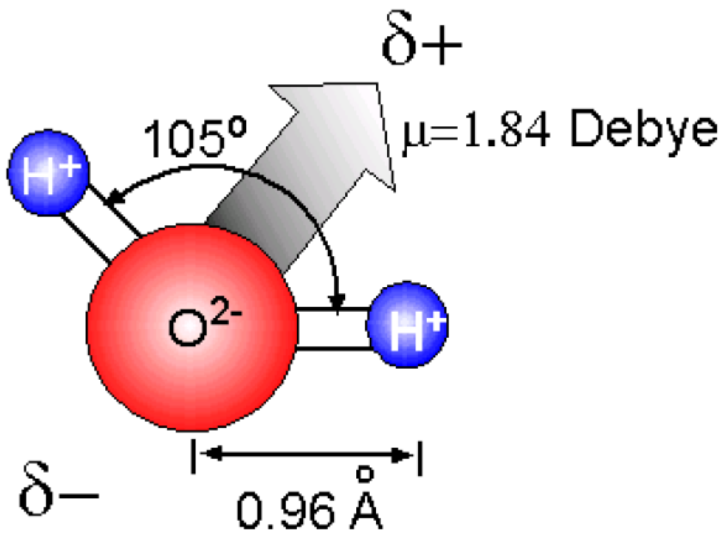
Basics of water quality

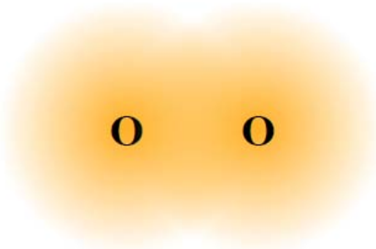
Water as a solvent

- **Structure of water: dipole**



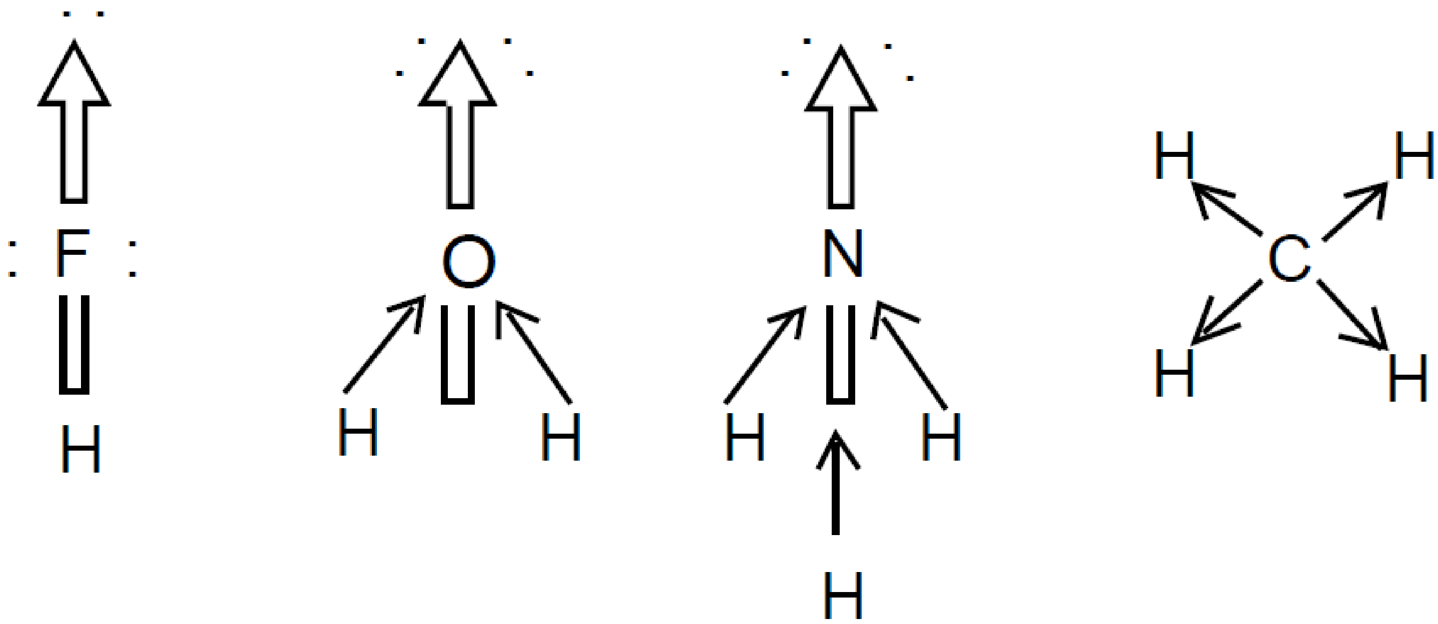
Dipole moment
A molecule has a dipole moment if the center of charge for the molecule's positive charges is ***NOT*** at the same spot as the center of charge for the molecule's negative charges

cf) O_2 – no dipole moment



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

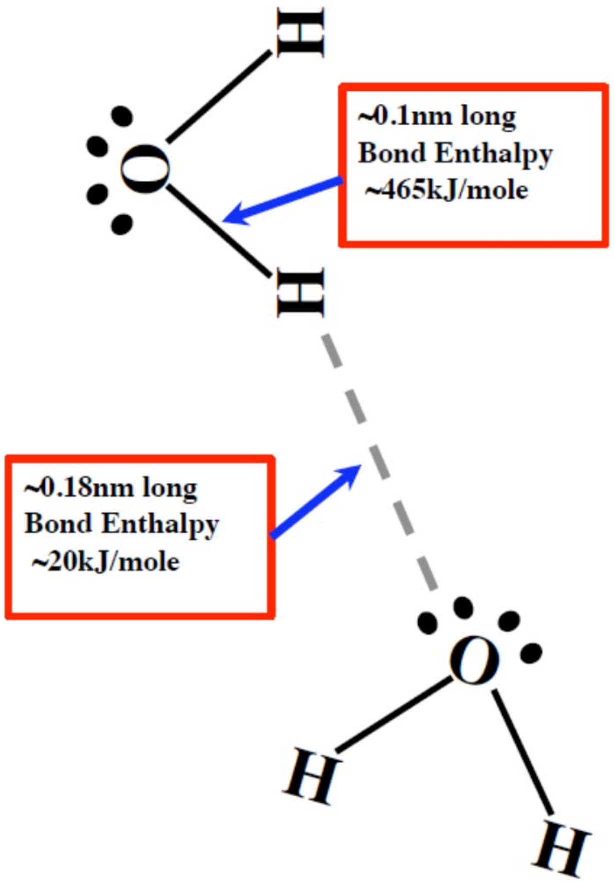
Water as a solvent



	Hydrogen fluoride	Water	Ammonia	Methane
Dipole moment	*1.91 D*	*1.84 D*	*1.30 D*	*0.0 D*

Water as a solvent

- **Hydrogen bonding**

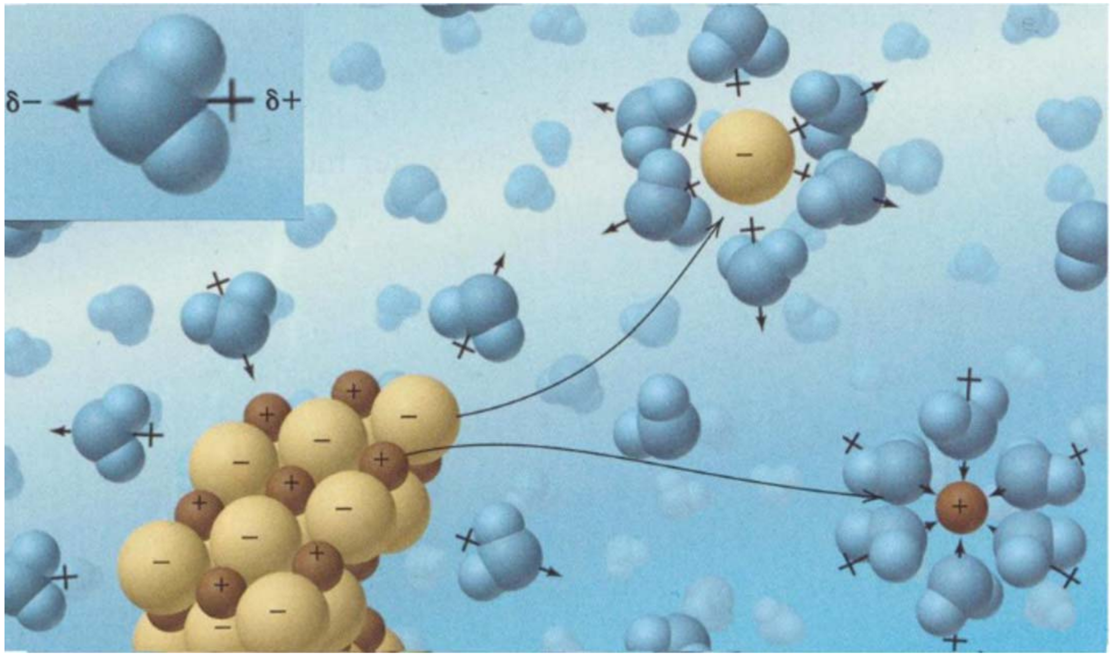


  - Weaker than covalent bond, but stronger than normal dipole-dipole interactions
  - Affect physical and chemical behavior of water in many ways

Water as a solvent

Property	H_2O	H_2S	CH_4	CH_3OH
Molecular weight	18	34	16	32
Dipole moment (Debyes)	2.0	0.9	0.0	1.7
Boiling point (℃)	100	-60	-161	65
Enthalpy of vaporization (kJ/g)	2.30	0.55	0.88	1.10
Melting point (℃)	0	-85	-181	-94
Enthalpy of fusion (kJ/g)	0.33	0.07	0.06	0.10

Water as a solvent



Tendency of water molecules to orient themselves around ions.

Benjamin (2002) Water Chemistry, McGraw-Hill

- High solubility for ions and polarized molecules

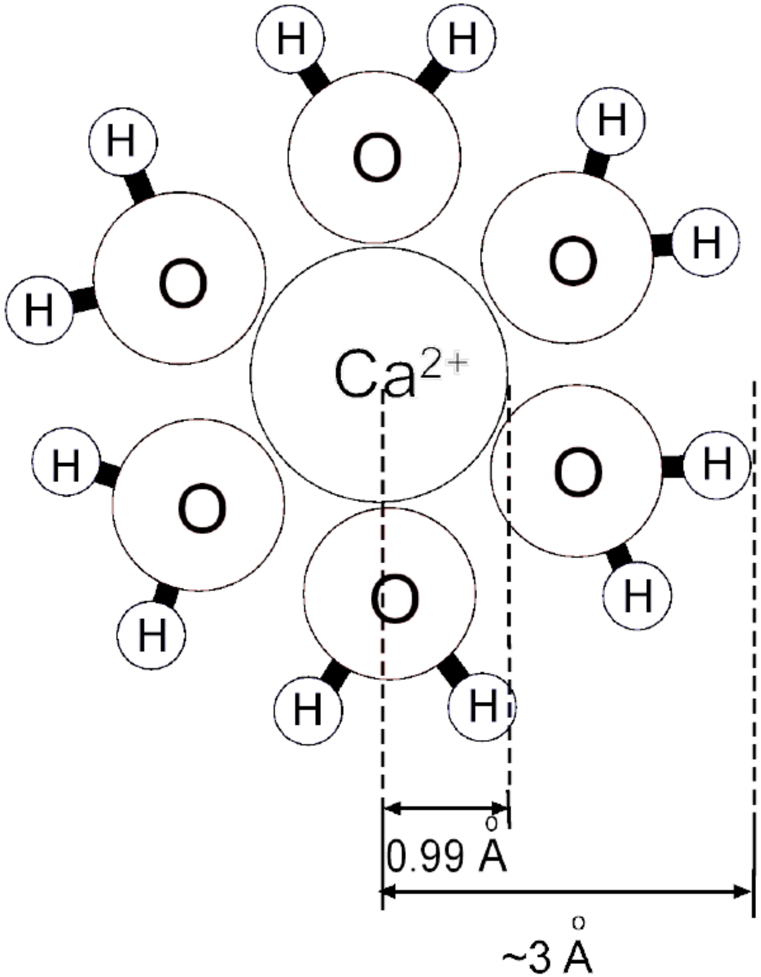
  ex) Na^+Cl^-, C_2H_5OH

- Low solubility for non-polarized molecules

  ex) high molecular weight hydrocarbons

- Hydrophilic vs. hydrophobic

Water as a solvent



- Metals are often dissolved in the form of hydrated ions
- Examples
  - $Na(H_2O)_4^+$
  - $Ca(H_2O)_6^{2+}$
  - $Fe(H_2O)_6^{3+}$
  - $Al(H_2O)_6^{3+}$

Concentration units

- Molality (*m*)

$$m, mole/kg = \frac{moles\ of\ solute}{1.0\ kg\ of\ solvent}$$

- Molarity (*M*)

$$M, mole/L = \frac{moles\ of\ solute}{1.0\ L\ of\ solution}$$

- Mass concentration

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

1.0 g/m^3 = 1.0 mg/L

→ common mass concentration unit

Concentration units

- Normality (*N*)

$$N, eq/L = \frac{equivalent\ of\ solute, eq}{1.0\ L\ of\ solution}$$

(meq/L more common)

Equivalent, eq = z x (moles of solute)
For acids, *z* is the number of replaceable hydrogen atoms; for oxidation-reduction reactions, *z* is the change in valence

* Equivalent mass

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

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 $CaCO_3$
  – Traditional unit for alkalinity and hardness

Note: $meq\ mass\ of\ CaCO_3 = 50\ \ mg/meq$

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

Other __as __
Nitrogen: mg/L as N
Phosphorus: % as P_2O_5
Potassium: % as K_2O

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:

$$x_A \cong \frac{n_A}{55.6}$$ *-- why 55.6??*

Other useful chemical relationships

- Electroneutrality principle

$$\sum cations\ (in\ eq/L) = \sum anions\ (in\ eq/L)$$

- Ionic strength

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

C_i = concentration of ionic species i (M)

z_i = charge of ionic species i

  - Significance: in dilute solutions (*I* ~< 10^{-3} M) the ions behave independently of each other, but as ion concentration increases, ion interactions become significant, <u>decreasing the activity</u> of the ions

Other useful chemical relationships

- Activity and activity coefficients
  - { } vs. [ ]

$$\{i\} = \gamma_i[i]$$

  - $\gamma_i \cong 1$ in dilute solutions (for most natural waters except for seawater)
  - But otherwise γ_i can be significantly smaller than 1
  - Güntelberg equation (for *I* < 0.1):

$$\log \gamma_i = -\frac{0.5{z_i}^2 I^{0.5}}{1 + I^{0.5}}$$

Other useful chemical relationships

- Equilibrium constant
  - For reversible reactions

$$aA + bB \rightleftharpoons cC + dD \quad \Rightarrow \quad K = \frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b}$$

  - In dilute solutions

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

Other useful chemical relationships

- Solubility product
  - Equilibrium constant for dissolution-precipitation reactions

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

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

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

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

$$C_g/C_s = H_u$$

C_g = concentration in gas phase (mg/L)
C_s = saturation concentration in liquid (mg/L)
H_u = unitless Henry's law constant

Water constituents

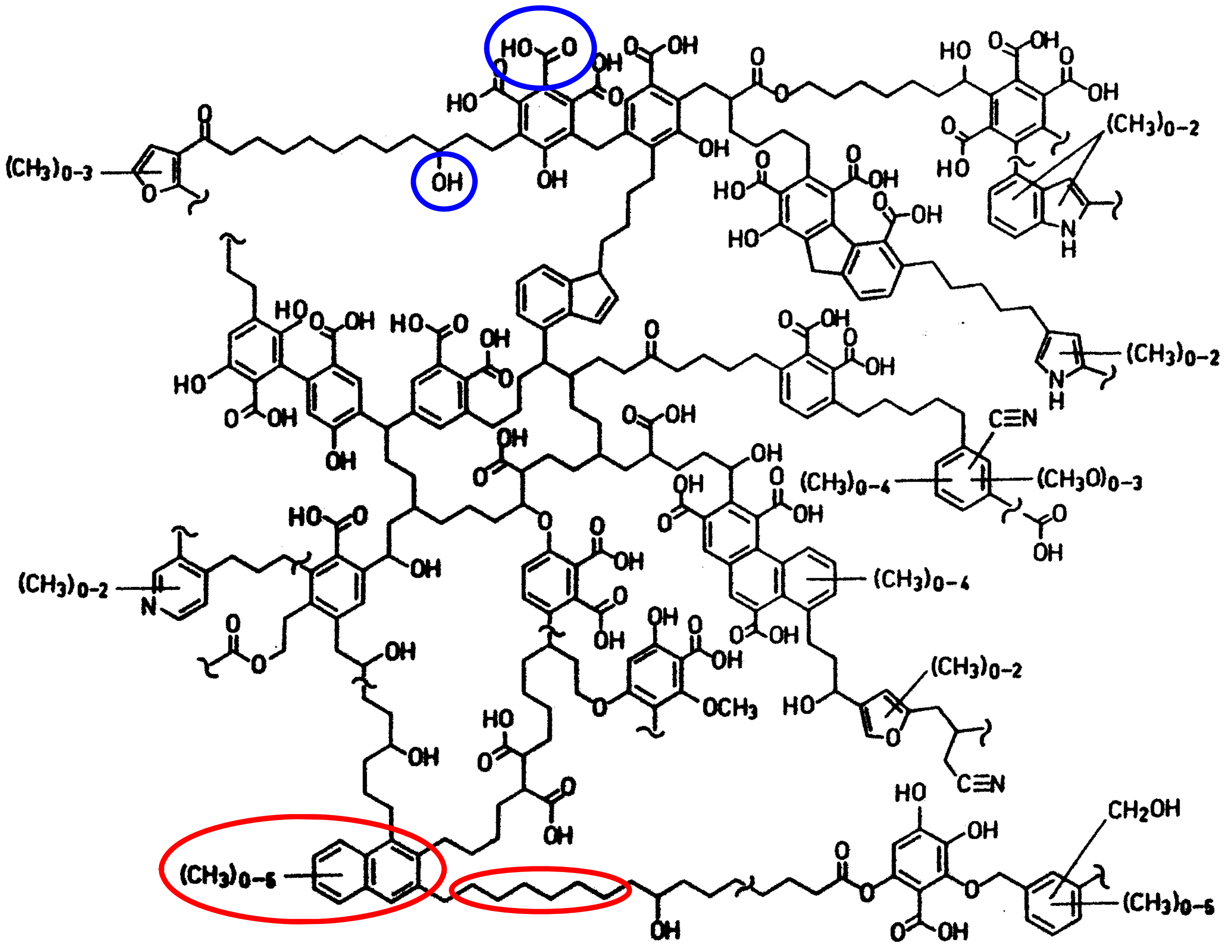
- **Dissolved inorganics**
  - Major in surface & ground water: Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, SO_4^{2-}, SiO_2 (mostly ionic)
- **Dissolved organic matter (DOM)**
- **Suspended matter**
- **Microorganisms**
  - attached/suspended
  - pathogenic/benign

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"!



hydrophilic

hydrophobic

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