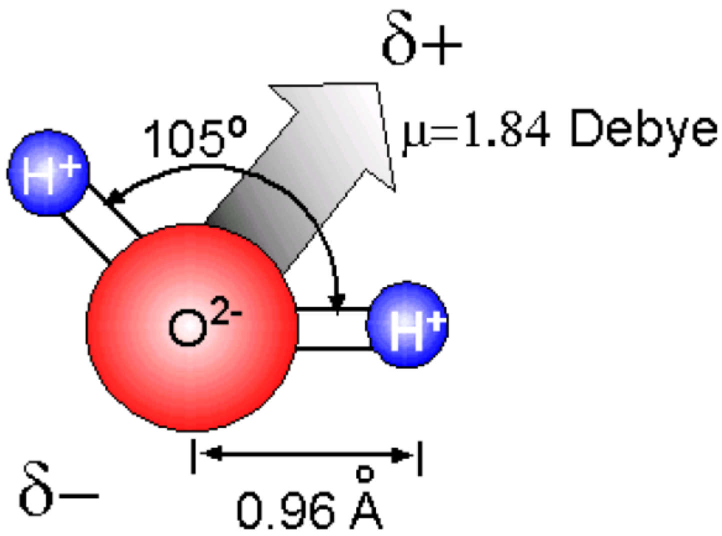
Basics of water quality

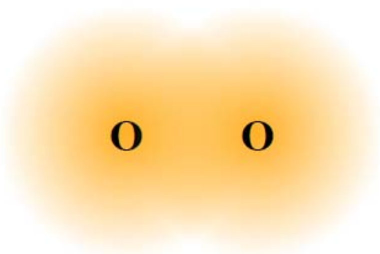
Water as a solvent

- **Structure of water: dipole**



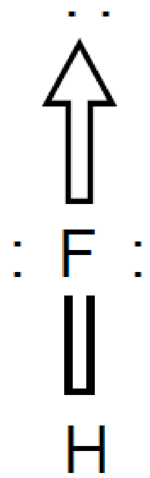
Dipole moment
A molecule has a dipole moment if the center of charge for the molecule's positive charges is ***NOT*** at the same spot as the center of charge for the molecule's negative charges

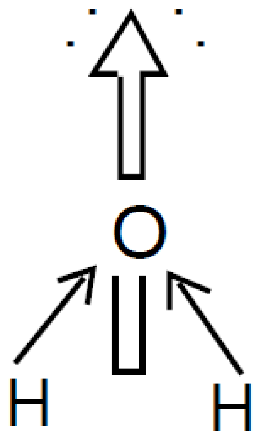
cf) O_2 – no dipole moment

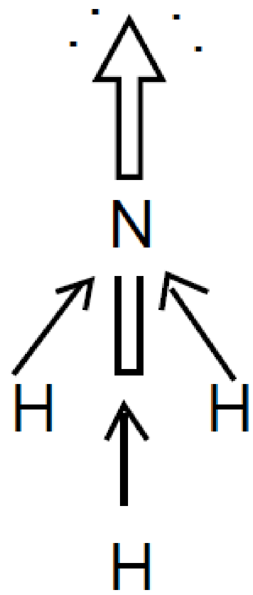


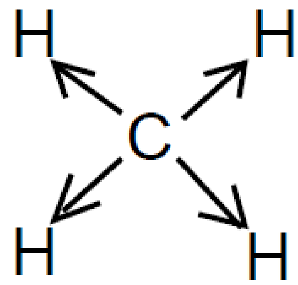
  - Highly polarized because of different electronegativity of O and H
  - (-) charge on O, (+) charge on H

Water as a solvent





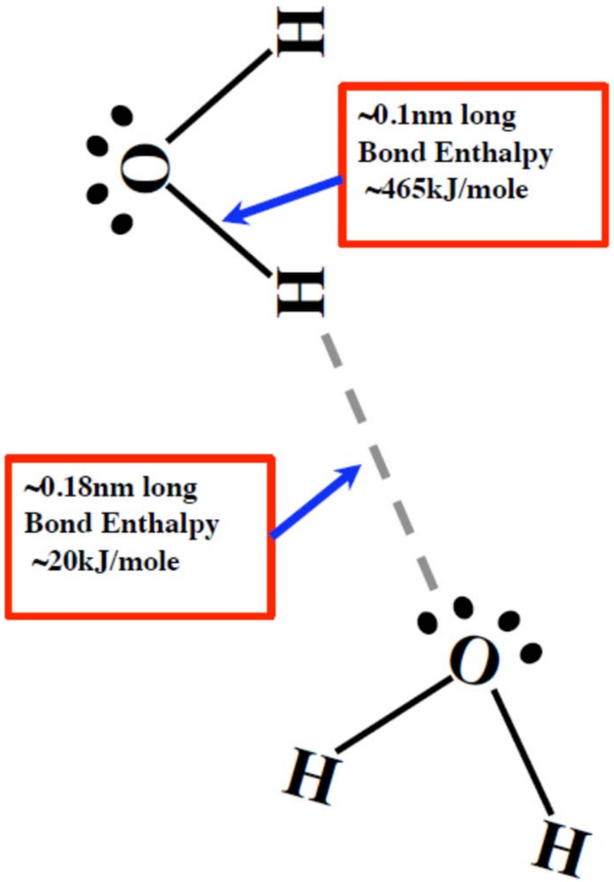




	Hydrogen fluoride	Water	Ammonia	Methane
Dipole moment	*1.91 D*	*1.84 D*	*1.30 D*	*0.0 D*

Water as a solvent

- **Hydrogen bonding**

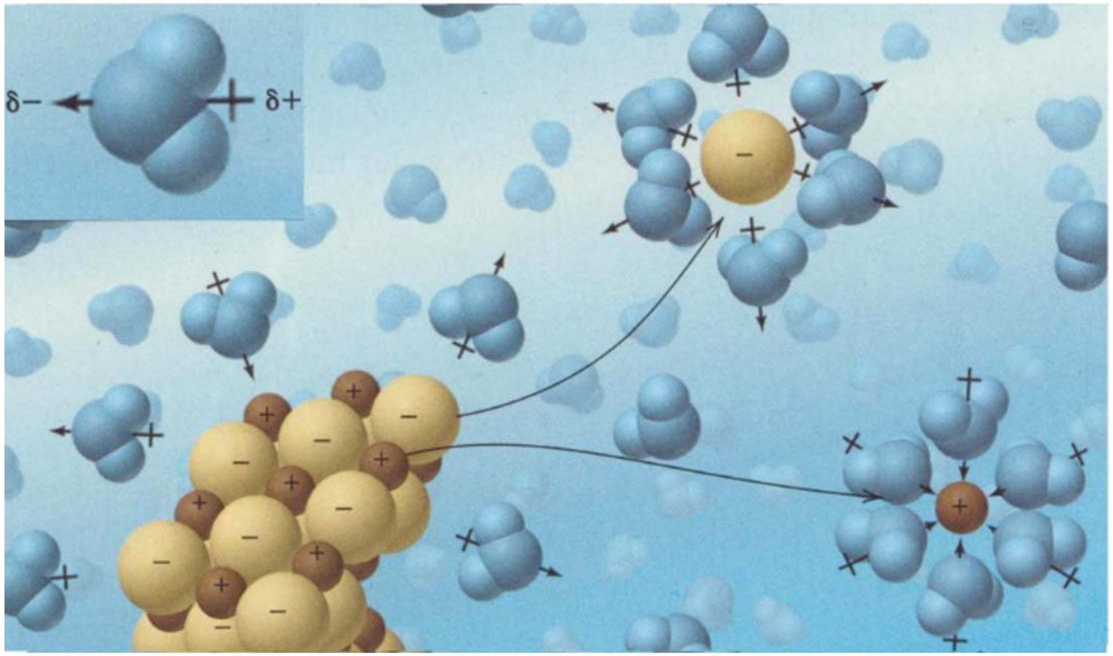


– Weaker than covalent bond, but stronger than normal dipole-dipole interactions
– Affect physical and chemical behavior of water in many ways

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

"Like dissolves likes"

- High solubility for ions and polarized molecules

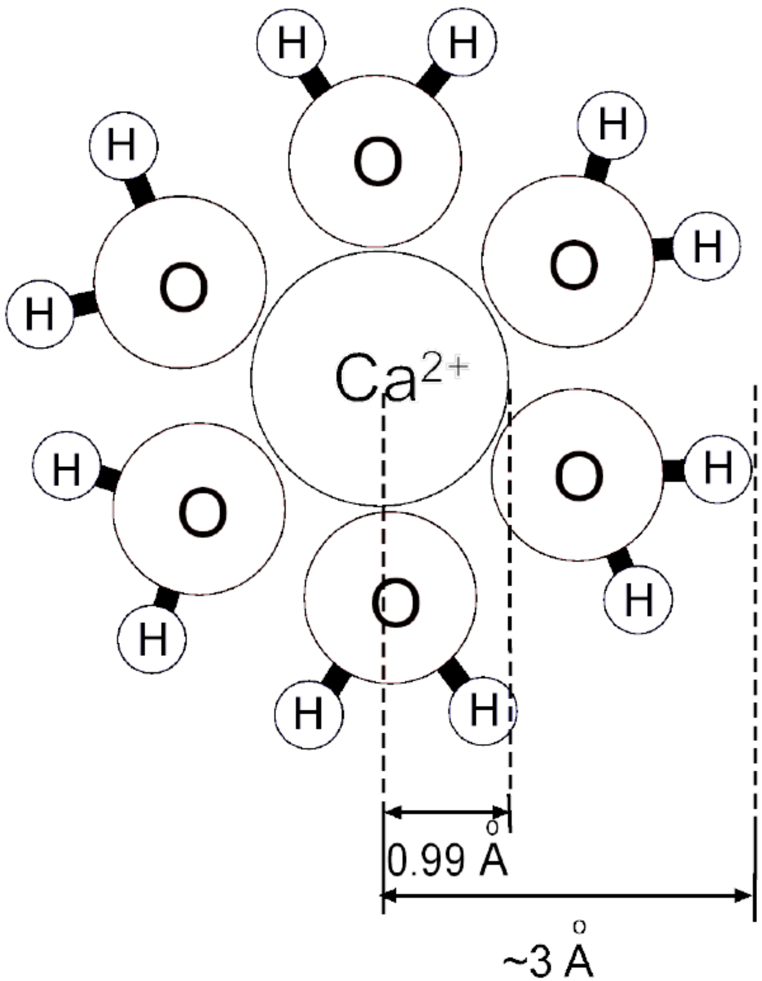
  ex) Na^+Cl^-, C_2H_5OH

- 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 (metal-aquo complex)

- 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 × (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, decreasing the activity 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) $CaCO_3 \rightleftharpoons Ca^{2+} + {CO_3}^{2-}$

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

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

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

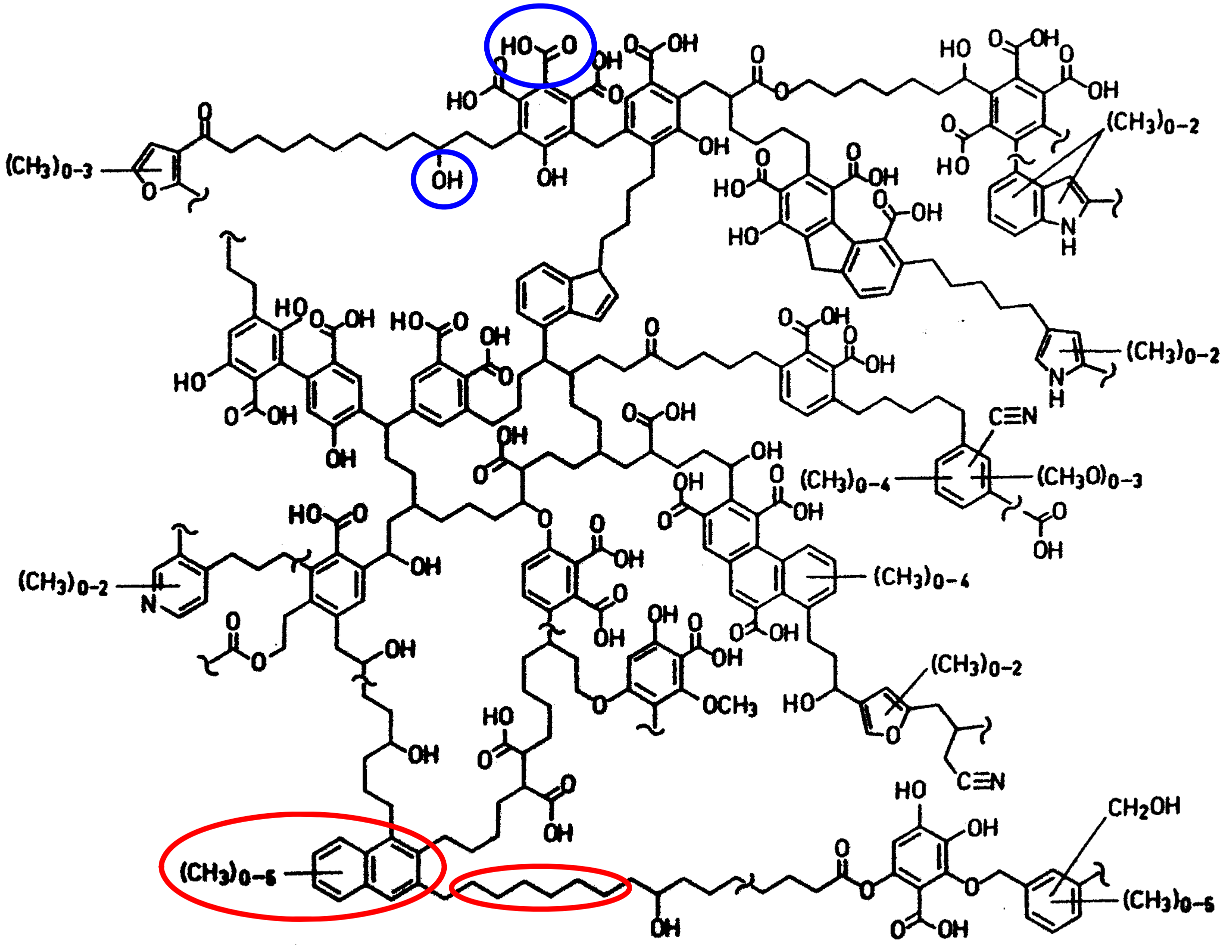
- **Dissolved inorganics**
  - Major in surface & ground water: Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, SO_4^{2-}, SiO_2 (mostly ionic)
- **Dissolved organic matter (DOM)**
- **Suspended matter**
  - Includes mineral colloids, microorganisms and their debris, organic polymers, …
  - Microorganisms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

Organics in natural waters

- **Simple sugars, amino acids, etc.**
  - Concentrations 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 >100,000
    - Hydrophilic/hydrophobic regions
    - Coat minerals, photoactive, affinity to metals & organics

Humic substances – representative structure

There's no humic "molecule"!



hydrophilic

hydrophobic

http://www.euni.de

Anthropogenic organic compounds in water

- >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