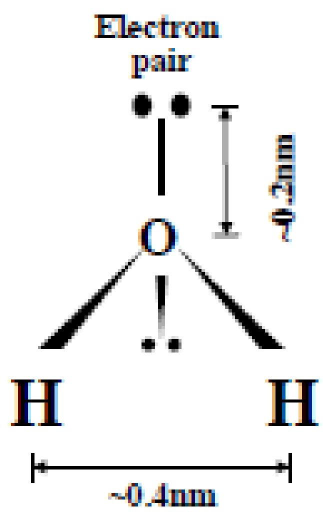
Uniqueness of water

Water – a unique solvent

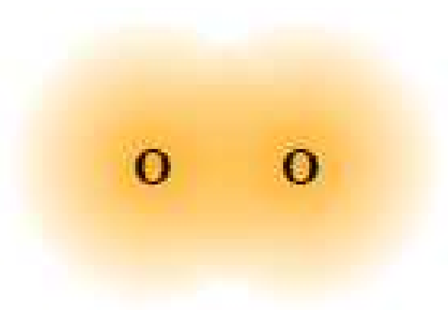
Property	H_2O	H_2S	CH_4	CH_3OH
Molecular weight	18	34	16	32
Dipole moment (Debyes)	2.0	0.9	0.0	1.7
Boiling point (°C)	100	-60	-161	65
Enthalpy of vaporization (kJ/g)	2.30	0.55	0.88	1.10
Melting point (°C)	0	-85	-181	-94
Enthalpy of fusion (kJ/g)	0.33	0.07	0.06	0.10



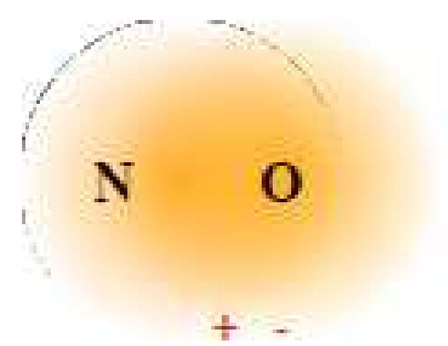
Dipole moment

A molecule has a dipole moment if the center of the molecule's positive charges is not at the same spot as the molecule's negative charges

O_2 – no dipole moment

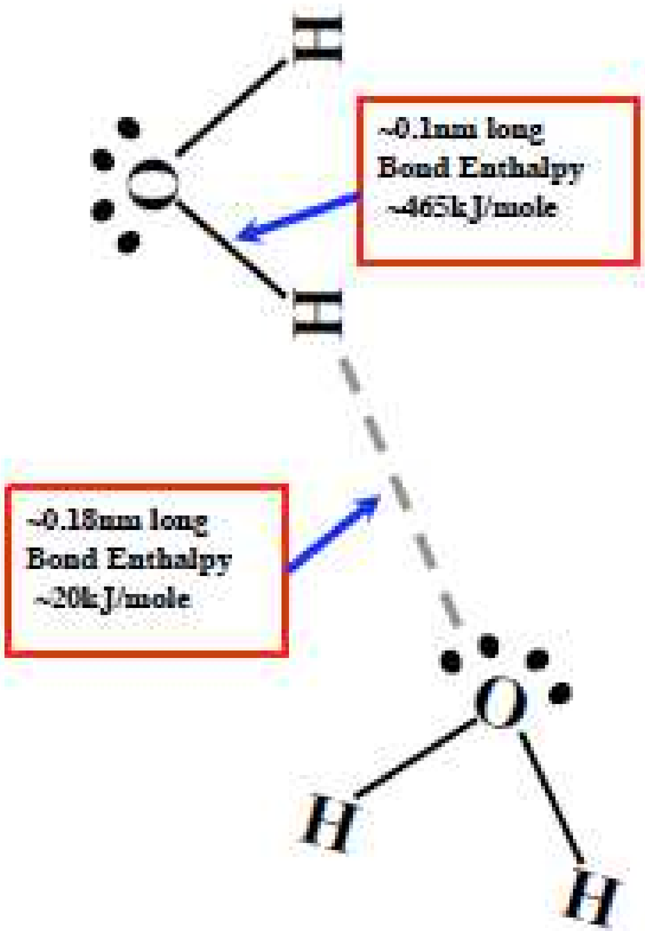


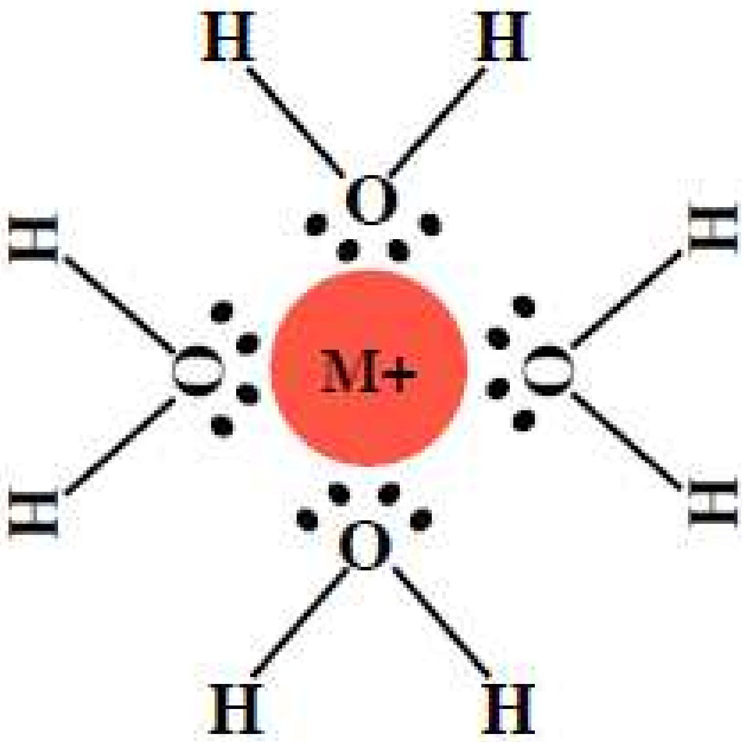
NO – dipole moment



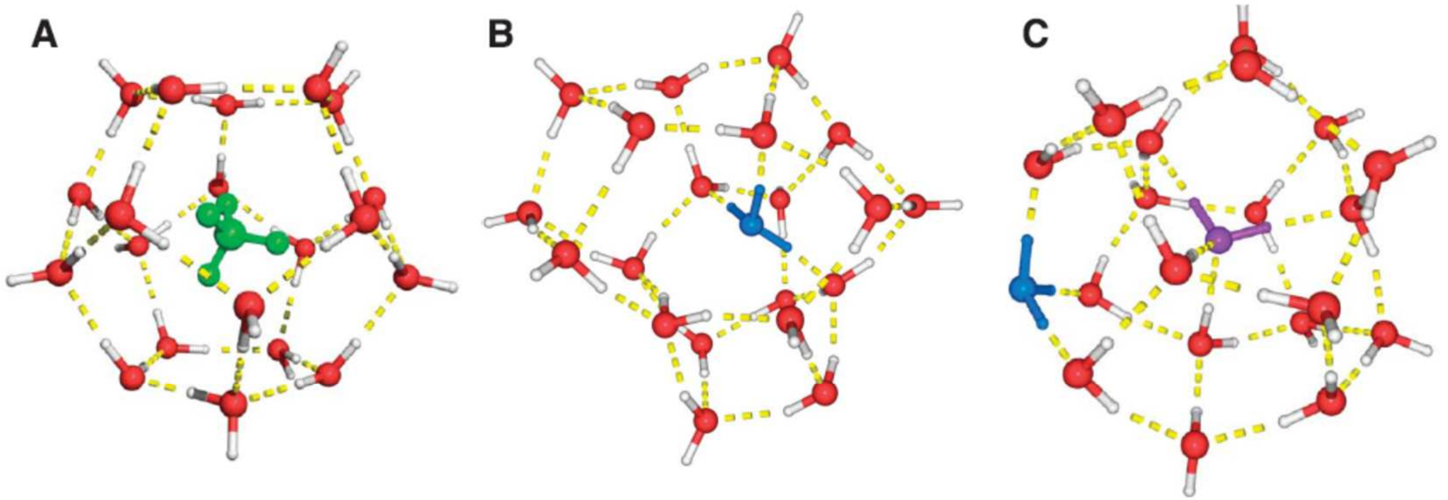
Electron density shifted to oxygen

Water – hydrogen bonding & dipole moment





Hydrogen bonding



Stable water clusters. (**A**) Methane clathrate consists of a dodecahedral water cage surrounding a methane molecule (green). The $n = 21$ protonated water cluster suggested by analogy has the H_3O^+ ion (blue) taking up a position inside the clathrate cage (**B**) or on its surface (**C**), displacing a neutral water molecule (purple) to the cage interior. The hydrogen bonds are indicated by the dashed lines in yellow.

Zweir, 2004, Science, 21:1119

- H_2O structure promotes incorporation of hydrogen bonding, polar, ionic entities
- Non-hydrogen bonding, non-polar, non-ionic entities disrupt water's structure

Basics of basics of water chemistry

Ionic strength, activity, molarity

- **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

- **Activity vs. molarity ({ } vs. [ ])**

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

  - $\gamma_i \cong 1$ in dilute solutions (for most natural waters except for seawater, this would be acceptable for crude calculations)
  - Güntelberg equation (for I < 0.1):

$$log_{10}\gamma_i = -\frac{0.5{z_i}^2 I^{0.5}}{1 + I^{0.5}}$$

Electroneutrality principle

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

** equivalent [eq] of an ion:*

(eq) = (mole) x (valence)

- **May use the following condition to determine the accuracy of water ion content analysis**

$$\left|\sum anions - \sum cations\right| \leq \left(0.1065 + 0.0155 \sum anions\right)$$

** ∑ values in meq/L*

Aqueous chemistry parameters

- **Units**
  - Mass/vol — kg/m^3, mg/L, …
  - #/vol — mole/L, # of organisms/mL
  - Transferable electrons or protons/vol — eq./L, meq./L
  - Mole fraction — mole/∑mole

- **Why different units?**
  - Engineers vs. chemists
  - Specific needs of the problem

Aqueous chemistry parameters

- **Aggregate parameters**
  - Characterize important properties of mixtures
    - __OD (oxygen demand)
    - TO__ (total organic carbons (C), halides (X))
    - Total hardness, Alkalinity, …
    - Total PCBs, Total PCTs, …
  - Conduct one analysis instead of many
- **__per__as__**
  - mg/L as $CaCO_3$ (for alkalinity & hardness)
  - mg/L as N
  - % as P_2O_5 or K_2O

Measures of (oxidizable) organic matter

- **BOD – Biochemical Oxygen Demand**
  - Measure of a water's biologically oxidizable constituents
    - Analyze [DO] in a water sample before & after controlled incubation
    - 5 day incubation is common
- **COD – Chemical Oxygen Demand**
  - Measure of a water's chemically oxidizable constituents
    - 2-3 hour reaction time
    - Generates liquid hazardous wastes
  - Does not oxidize organic N
- **TOC, DOC – Total/Dissolved Organic Carbon**
  - Measure of a water's organic carbon content
    - Analyze mass/concentration of CO_2 produced after chemical oxidation of a sample
    - Sampling time – a few minutes

BOD_5 vs COD vs TOC

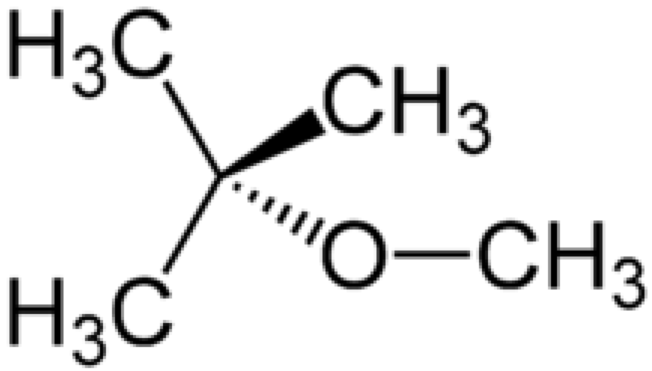
Compound	Formula	MW	BOD_5	COD	TOC	COD/TOC	TOC/MW	COD/MW
Methane	CH_4	16	??	64	12	5.3	0.75	4.0
MTBE	$C_5H_{12}O$	88	~0	240	60	4.0	0.68	2.7
Benzene	C_6H_6	78	??	240	72	3.3	0.92	3.1
Glucose	$C_6H_{12}O_6$	192	~192	192	72	2.7	0.38	1.0

$$CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O$$

$$C_5H_{12}O + 7.5O_2 \Leftrightarrow 5CO_2 + 6H_2O$$

$$C_6H_6 + 7.5O_2 \Leftrightarrow 6CO_2 + 3H_2O$$

$$C_6H_{12}O_6 + 6O_2 \Leftrightarrow 6CO_2 + 6H_2O$$



[MTBE]

pH

$$pH = -\,log_{10}\,\{H^+\} \;\approx\; -\,log_{10}\,[H^+]$$

- For most natural waters, $5 < pH < 9$
  - Most aquatic life adapted for this range

- Self ionization constant of water, K_w

$$K_w = \{H^+\}\{OH^-\} = 10^{-14}$$

$$pK_w = pH + pOH = 14$$

@ 25 °C

- Chemical speciation can be highly pH dependent

$$ROH \;\Leftrightarrow\; RO^- + H^+$$

$$K_a \approx \frac{[RO^-][H^+]}{[ROH]}$$

  - If pH < pK_a, protonated (associated)
  - If pH > pK_a, deprotonated (dissociated)