

# 1. Intro and the Properties of Water

Every water analysis, or set of analyses, tells a story: where the water came from, how old it is, what rocks have dissolved or precipitated, what are the biologic interactions, and what has been the human impact.. The objective of the course is to provide the students with sufficient background in the theory of geochemical reactions, and enough practice with example problems, to be able to hear and understand the story told by a water analysis.

## 1.1. Physical Properties Of Water:

The study of chemical hydrogeology is largely the study of how solids and solute interact in, and with, water. With the exception of direct evaporation of a volatile compound, and the direct photodegradation of a pure compound, all other processes must account for water, either as a solvent, a reactant, or a competitor. Knowledge of the physical and chemical properties of water, therefore, is fundamental to an understanding of aquatic chemistry.

The key properties of water are dipole moment, dielectric constant, heat capacity, and its ability to both donate and accept protons. This imparts on water the ability to hydrogen bond with itself, to hydrogen bond with both proton donors and proton acceptors, to dissociate, to coordinate with ions and other dipoles, and to store and transport heat.

Property	Value
Molar mass	18.015;
Molar Volume	55.5 moles/liter
Boiling Point (BP)	100°C at 1 atm
Freezing point (FP)	0°C at 1 atm
Triple point	273.16 K at 4.6 torr
Surface Tension	73 dynes at 20°C
Vapor pressure	0.0212 atm at 20°C
$\Delta H$ of vaporization	40.63 kJ/mol
$\Delta H$ of Fusion	6.013 kJ/mol
Heat Capacity (cp) ,	4.22 kJ/kg·K
Dielectric Constant ( $\epsilon$ )	78.54 at 25°C
Viscosity	1.002 centipoise at 20°C
Density	1 g/cc
Density maxima	4°C

Table 1-1: Key Physical Properties of Water

The basic structure of a water molecule is well known:

- O--H bond length = 95.7 picometers
- H--O---H angle = 104.5°
- O-H bond energy = 450 kJ/mol
- Dipole moment = 1.83 debyes

The structure of liquid water, however, is still debated, and to understand solubility, an understanding of water structure, and hydrogen bonding is necessary.

### 1.1.1. Hydrogen Bonding:

(View the MPEG movied of glycine and water hydrogen-bonding:

<http://www.cm.utexas.edu/movies/wssp/>

- Hydrogen bonding between liquid water molecules explains many of the physical and chemical properties. Hydrogen bonding in liquid water allows water to *self-associate*, which significantly changes its behavior. The strong hydrogen bonding in water explains

why water has such a high melting and boiling point, high latent heat of condensation and crystallization, and low vapor pressure, for example.

- The Hydrogen Bond is a bond formed between a *hydrogen donor* and a *hydrogen acceptor*, a molecule with non-bonding *lone-pair electrons*. In natural waters, the acceptor is an oxygen, nitrogen, or fluoride atom.
- Linus Pauling had the first theoretical approach to H bonds, stating that they were electrostatic in nature. On the basis of the electrostatic model, Pople calculated the bond energy of the H bond in a linear water dimer to be about 6 kcal/mol. The strength of the bond was found to be related to the angle formed by the X---H bond, and the direction of the Y lone pair. The energy of the system is increased with increasing angle phi by  $k(1-\cos \phi)$ .
- H bond energy contributions:
  1. **Electrostatic attraction:** Dominant in long range, or non-directional bonds
  2. **Delocalization energy:** charge transfer from the proton donor to the proton acceptor. Dominant in strong, directional, H bonds,  $\sim 1/20$ th of an electron charge.
  3. **Dispersion**
  4. **Exchange repulsion.**
- Water Polymers:
  - a) The average water H bond energy in the trimer is higher than in the linear dimer, and remain the same for higher polymers. This is a consequence of reinforcement of the charge transfer. Energy is approximately 2.4 times that of one H bond.
  - b) A cyclic structure of water is therefore probably formed, leaving a central void space.

### 1.1.2. Structure Models:

Several models of the structure of water have been proposed, each attempting to match either experimental evidence from spectroscopy, or modeling results.

*Ice I:*

- Tetrahedrally coordinated regular structure requiring 6 units to return to the origin.
- O...O distances are all equal at 2.76 Å.
- The protons lie exactly in the O---O plane

*Flickering cluster model*

- Clusters of structured bonding form and break apart within a matrix of unstructured molecules (Nemethy and Scheraga, 1964).

*Broken ice model:*

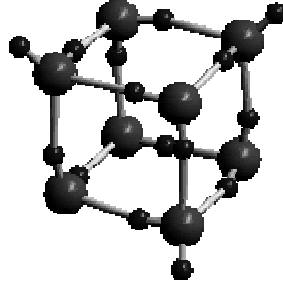
- After ice melts, the basic structure is retained, and each water is bonded to 4 others.

*Network structure*

- Most probable overall structure for cold water,
- Consists for the most part of hydrogen bonded, four-coordinated, framework regions, with interstitial monomers occupying some fraction of the cavities the framework encloses.
- The geometry is probably more random as the water gets warmer. There is in all the structures a certain amount of randomness.

The best guess:

- Two general environments of water exist: H bonded and loose monomers of broken bonds.
  - 1) The bonded regions are "bulky", the loose are "dense". The denseness and bulkiness can probably not be segregated into patches



- 2) The bulky water contains unoccupied interstitials, The dense water is occupied interstitials ("self clathrates), with central, non-hydrogen bonded monomers.
- 3) The life-time of these structures is short, with dense patches forming and dissolving rapidly. The lifetime of a dense area decreases with increasing T, resulting in an increase in water density. As T decreases, the bulky form predominates.

## 1.2. Composition of Water

### 1.1.3. Seawater:

The oceans account for 97.13% of the worlds water, and can be generalized as a 1.1 molar solution of solutes with the average composition of:

- The composition of seawater varies with location and depth, with higher total solutes found in colder polar waters, and with large changes in non-conservative elements with depth due to biological processes.
- Seawater chemistry, and the chemistry of saline waters and brines, will be covered toward the end of the course, depending on time.

Element	Major Species	Conc. (mg/kg)	Conc. Molal
Chloride	Cl <sup>-</sup>	19,350	
Sodium	Na <sup>+</sup>	10,760	
Sulfur	SO <sub>4</sub> <sup>2-</sup>	2,710	
Magnesium	Mg <sup>2+</sup>	1,290	
Calcium	Ca <sup>2+</sup>	411	
Potassium	K <sup>+</sup>	399	
Carbon	HCO <sub>3</sub> <sup>-</sup>	142	
Bromide	Br <sup>-</sup>	67	
Strontium	Sr	8	
Boron	BO <sub>4</sub> <sup>3-</sup>	4.5	
Fluorine	F <sup>-</sup>	1.3	
Silicon	H <sub>4</sub> SiO <sub>4</sub>	0.5-10	
DOC	C	0.3-2	
TDS		34,500	
Hydrogen	H <sup>+</sup>	10 <sup>-8.35</sup>	

### 1.1.4. Composition of the Atmosphere:

- The atmosphere represents a major reservoir of water - not so much in volume as in time and contact.

- Consequently, natural waters often carry the signature of the atmosphere with respect to dissolved gases and some solutes. Gas dissolution will be covered when we look at the carbon dioxide system and Henry's Law
- The atmosphere is the major source of molecular oxygen, the primary electron acceptor for biologic processes.
- Whether or not a water is open to the atmosphere is often an important question, and a major goal for ground water evaluation

Element	Primary Species	% (v/v)	ppm (v/v)
Nitrogen	N <sub>2</sub>	78.1	781,000
Oxygen	O <sub>2</sub>	20.9	209,000
Water	H <sub>2</sub> O	0.1-2.8	1,000-28,000
Argon	Ar	0.93	9,300
Carbon	CO <sub>2</sub>	0.037	370
Neon	Ne		18
Helium	He		5.2
Methane	CH <sub>4</sub>		1.75
Krypton	Kr		1.1
Carbon	CO		~1.0
Sulfur	SO <sub>2</sub>		1.0
Nitrogen	N <sub>2</sub> O		0.5
Hydrogen	H <sub>2</sub>		0.5
Ozone	O <sub>3</sub>		0.01-0.1
Xenon	Xe		0.087

### 1.1.5. Composition of Rain and Snow:

- Rain and snow chemistry is highly variable, and reflect multiple inputs from the atmosphere. Sea-spray, and continental dust.
- Determining the composition of rain and snow is a fundamental step in evaluating the reaction path a certain water has taken, and rain or snow should never be assumed to be simply distilled water. For some waters, atmospheric input is the only source for sulfate and chloride.
- In some areas, such as the New England and Norway, atmospheric contamination by acid gases results in extremely low pH rain water, significant input of sulfate, nitrate, and chloride, and the secondary mobilization of aluminum in receiving waters, resulting in Al toxicity in fish.

Species	Sierra. Snow	N.C. VA Rain	Menlo Park Rain
Ca <sup>2+</sup>	0	0.65	0.8
Mg <sup>2+</sup>	0.2	0.14	1.2
Na <sup>+</sup>	0.6	0.56	9.4
K <sup>+</sup>	0.6	0.11	0
NH <sub>4</sub> <sup>+</sup>	0		
HCO <sub>3</sub> <sup>-</sup>	3.0		4.0
SO <sub>4</sub> <sup>2-</sup>	1.6	2.18	7.6
Cl <sup>-</sup>	0.2	0.57	17
NO <sub>2</sub> <sup>-</sup>	0.02		0.02
NO <sub>3</sub> <sup>-</sup>	0.1	0.62	0
pH	5.6		5.5

### 1.1.6. Composition of Rivers and Lakes

- The composition of a river, and eventually a lake, is a reflection of four inputs: atmospheric input of gases and solutes, biologic processes, discharge of ground water, and local interactions with mineral components in the soil or stream bed.
- At baseflow, the water in a gaining river is derived from ground water!!, so the composition of the river is really a reflection of the aquifer, while for a losing stream the reverse holds - the composition of the shallow ground water reflects the river, for example an alluvial aquifer.

Species	HSS	Dorsero	Camero	Asco	Hite	Lees F
CFS	244	2399	4138	7639	14167	17550
Ca <sup>2+</sup>	16	48	56	70	73	76
Mg <sup>2+</sup>	3.1	9.8	12	25	26	25
Na <sup>+</sup>	5.9	40	62	79	79	74
K <sup>+</sup>	1.6	2.2	3.4	3.6	3.5	4.0
HCO <sub>3</sub> <sup>-</sup>	72	120	142	178	182	184
SO <sub>4</sub> <sup>2-</sup>	6.0	77	93	281	230	235
Cl <sup>-</sup>	1.3	54	84	11	43	48
B	0	0	0.04	0.08	0.12	0.11
TDS	91	334	400	660	658	580

- The composition of a river is a dynamic thing, with concentrations generally (but not always) increasing down stream, but pH generally increasing, for example, the Colorado River, 1960's:

### 1.3. UNITS AND TERMINOLOGY

**TDS:** Total Dissolved Solids.

Fresh Water: <1000 mg/l TDS

Brackish Water 1000 - 20,000 mg/l TDS

Saline Water: ~Seawater, or 35,000 mg/l TDS

Brines: >35,000 mg/l TDS

**Hardness** Concentration of Mg and Ca, often expressed in CaCO<sub>3</sub> equiv.

**Conductivity** (Specific Conductance): Inverse of electrical resistance.

**Molality** (m) moles perKg solvent

**Molarity** (M) moles per liter of solution

**GFW** Gram Formula weight: grams per mole

**System** A group of chemicals (i.e. gas, minerals, water) we wish to consider

**Species** The specific form an element takes, a chemical entity

#### 1.1.7. Mass Concentration:

**Method 1:** mass solute/unit volume of solvent (W/V)

$$1) \text{ mg/l} = \text{ug/ml} = \text{g/m}^3$$

$$2) \text{ ug/l} = \text{ng/ml} = \text{mg/m}^3$$

**Method 2:** Weight of solute/unit weight of solvent

$$1) \text{ ppm} = \text{mg/Kg} = \text{g/tonnes} = \text{ug/g}$$

$$2) \text{ ppb} = \text{ug/Kg} = \text{mg/Tonnes} = \text{ng/g}$$

- *When the density of the solvent is equal to 1 Kg/l, than the two methods of expression are equivalent.*
- For most dilute waters, the two are sufficiently close to be operationally interchangeable. This is not the case for some brackish waters, and sea water and most brines. For these waters, the w/w basis should always used.
- For analytical geochemistry, it is preferable to use the w/w basis, even though it is more common to find analyses expressed on a mg/l basis.
  - 1) w/w basis is ALWAYS use for sediments and soils.

### 1.1.8. Alternative terms of Mass Concentration

#### *Common constitution conversion*

1) given a solution of 360 mg/l NH<sub>4</sub><sup>+</sup>, and 1240 mg/l NO<sub>3</sub><sup>-</sup>, the common ion is N. So:

$$\text{mg NH}_4\text{-N/l} = 360 \text{mg NH}_4/\text{l} \times \frac{14 \text{mg N}}{18 \text{mg NH}_4 \text{ (i.e., x Mole\%)}} = 280 \text{ mg/l NH}_4\text{-N}$$

$$\text{mg NO}_3\text{-N/l} = 1240 \text{ mg NO}_3\text{-/l} \times \frac{14 \text{ mgN}}{62 \text{ mg NO}_3} = 280 \text{ mg/l NO}_3\text{-N}$$

- This is useful only when it is desired to find the concentration of the total amount of the common constituent, at other times it is a supreme irritation.
- It is very commonly used for N and P analyses of waters and waste waters, and by oceanographers, and may or may not be properly identified as such, so be careful.

### 1.1.9. Molar Concentration and Activity:

**Molarity:** (*M*, mol/L) *The number of moles of a specific species per liter of solution.*

This method is used in order to express ALL constituents in comparable units. These units are also used for equilibrium calculations.

1) 1 molar solution = 1 mole/l = g/l x formula weight

2) \*\*1 mmolar = 1 mmole/l = mg/l x formula weight

**Molality:** (*m* (mol/kg)) *The number of mols of a specific species per kilogram of solvent.*

Units of molality are particularly convenient when one does not want to have to worry about changes in volume that might occur due to temperature, pressure, and/or composition, such as with seawater

3) \*\*1 mmolal = 1 mmole/Kg = ppm x formula weight

**Normality** (*N*, equivalents/L) *The number of equivalents of acid, base, or redox-active species per liter of solution.*

This method is used in order to equate the reaction potential of polyvalent ions.

$$\text{Equivalent weight} = \frac{\text{molecular weight}}{\text{ion charge}}$$

$$\text{Normality} = \text{equivalents/l} = \frac{\text{mass/l}}{\text{equivalent weight}}$$

**Mole Fraction** (*X*, dimensionless): *The fractional concentration of a specific species where the fraction is computed based on a knowledge of the numbers of mols of all of the species present.*

### 1.1.10. Mass concentration as CaCO<sub>3</sub>:

- This is a common system of expressing both the hardness and the alkalinity of a water or waste water. The advantages derive mainly from waste water engineers, for which CaCO<sub>3</sub> was a common reagent, and further, the GFW was conveniently 100.
- For everyone else, this system is a continuous hassle, and in this class we will deal exclusively in meq alkalinity, or mg/l HCO<sub>3</sub><sup>-</sup>. We will not deal with hardness at all.
- The equation is: **meq/l alkalinity x 50 mg CaCO<sub>3</sub>/meq = mg/l alk. as CaCO<sub>3</sub>**