Chemical Oceanography

Dr. David K. Ryan

Department of Chemistry

University of Massachusetts Lowell

&

Intercampus of Marine Sciences Program

http://sites.uml.edu/David-Ryan/teaching/chem-6530

Websites of interest Re: H_2O

- www.biology.arizona.edu/biochemistry/tutorials/chemistry/page3.html
- www.science.uwaterloo.ca/~cchieh/cact/applychem/waterchem.html

These websites appear to have accurate information, however it is impossible for me to verify details or guarantee availability.

Website for Millero 2013

http://fig.cox.miami.edu/~lfarmer/MSC215/MSC215.HTM

Monterey Bay Aquarium Research Institute (MBARI)

www.mbari.org/chemsensor/pteo.htm

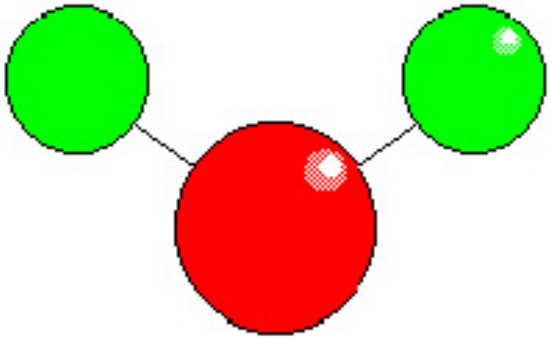
Water – Amazing Stuff

Chemical Oceanography

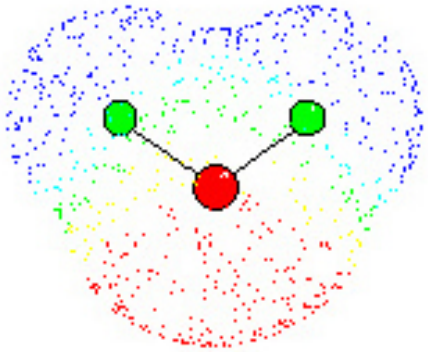
Physical Chemistry of Seawater (E&H Chap. 3)

- Seawater is 96.5 % H_2O
- Water unique substance & solvent
- Review structure
- Discuss selected unusual properties
- Consequences of water anomalies
- Phase diagrams

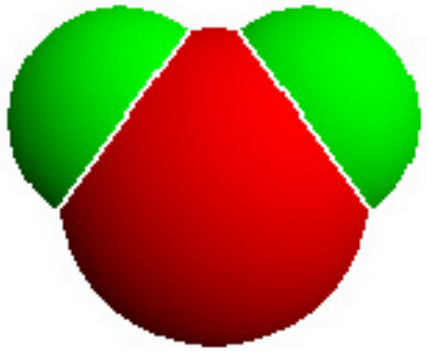
Molecular Structure of H_2O



"Ball & Stick" Model



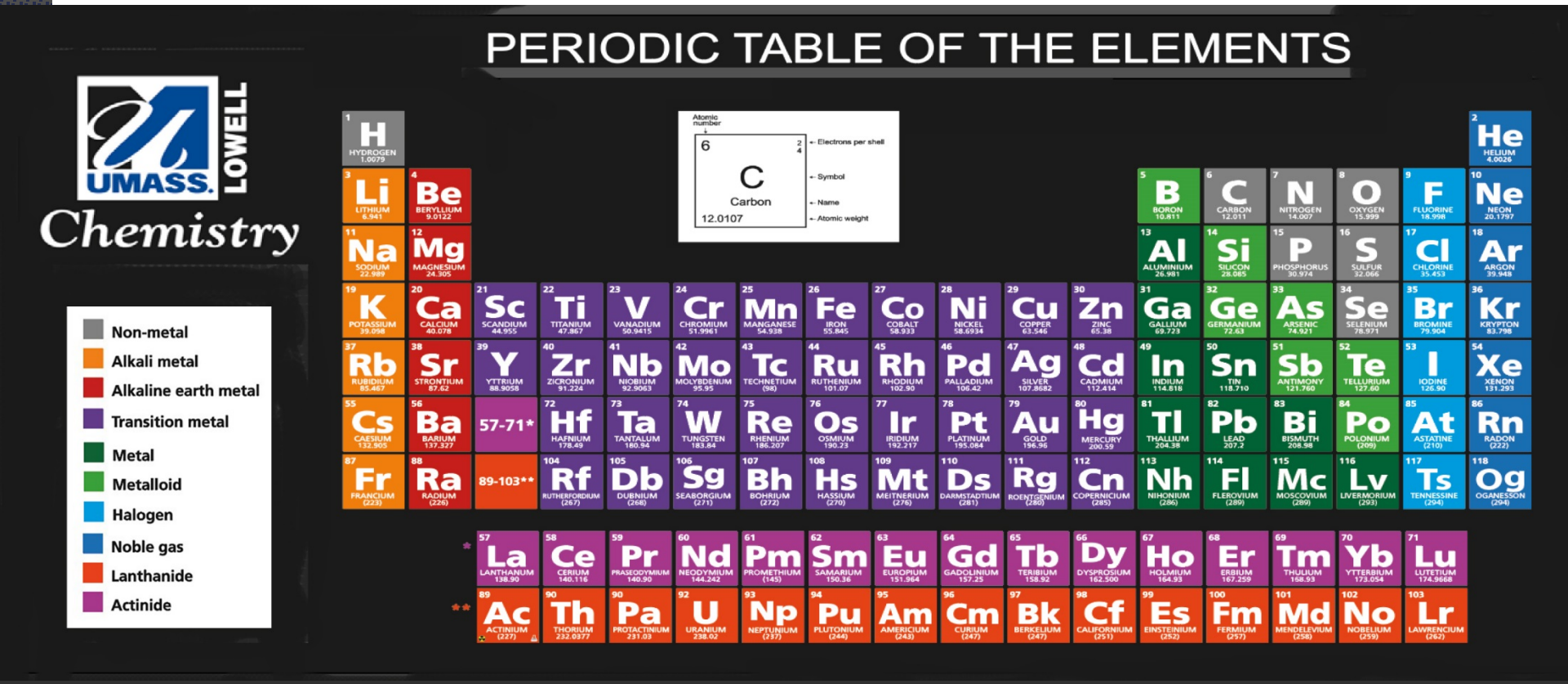
Electron Density Distribution



Space Filling Model

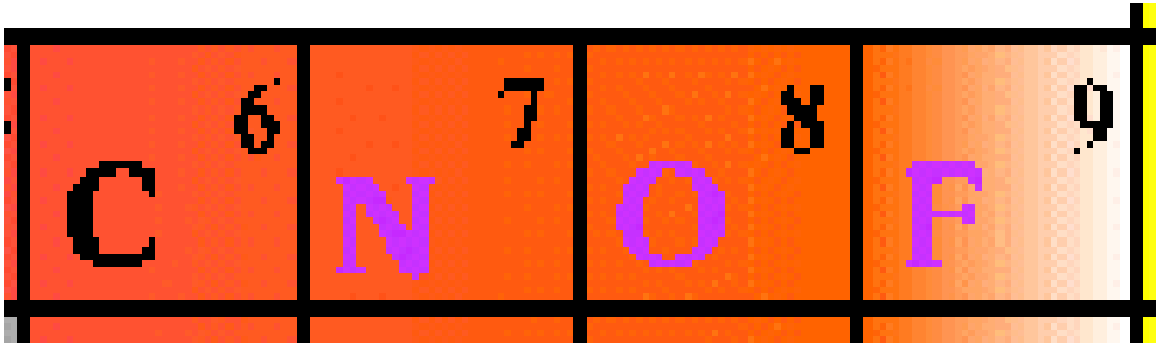
Periodic Table of the Elements

Rows = Periods
Columns = Groups or Families



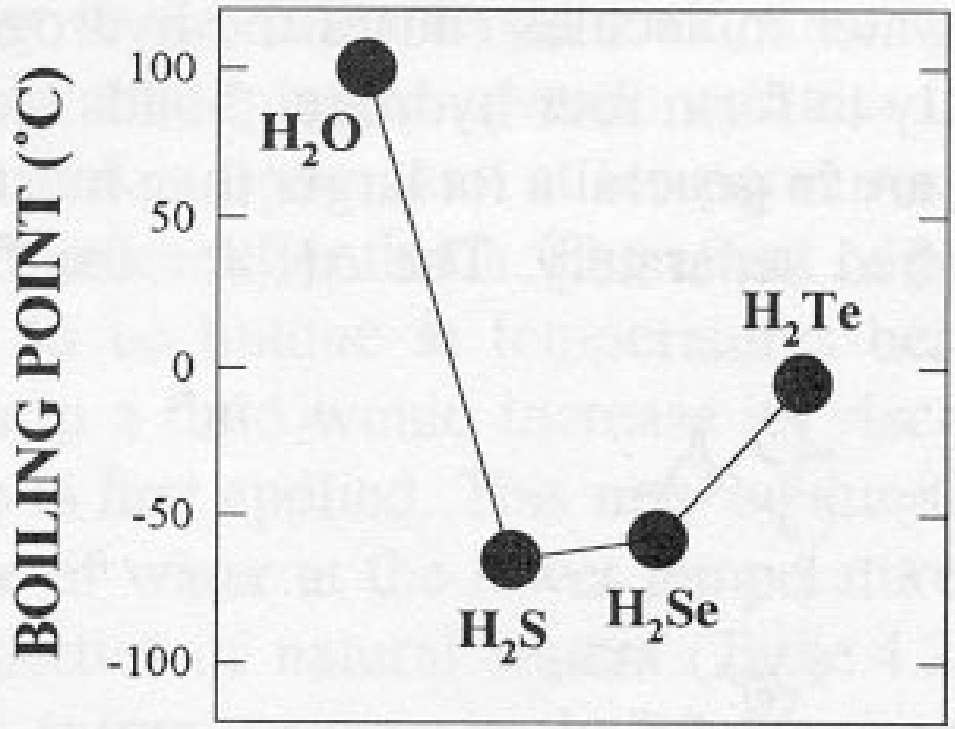
Zoom in on O and its neighbors

Part of one period



Each can form compounds with hydrogen

Boiling Point Comparison



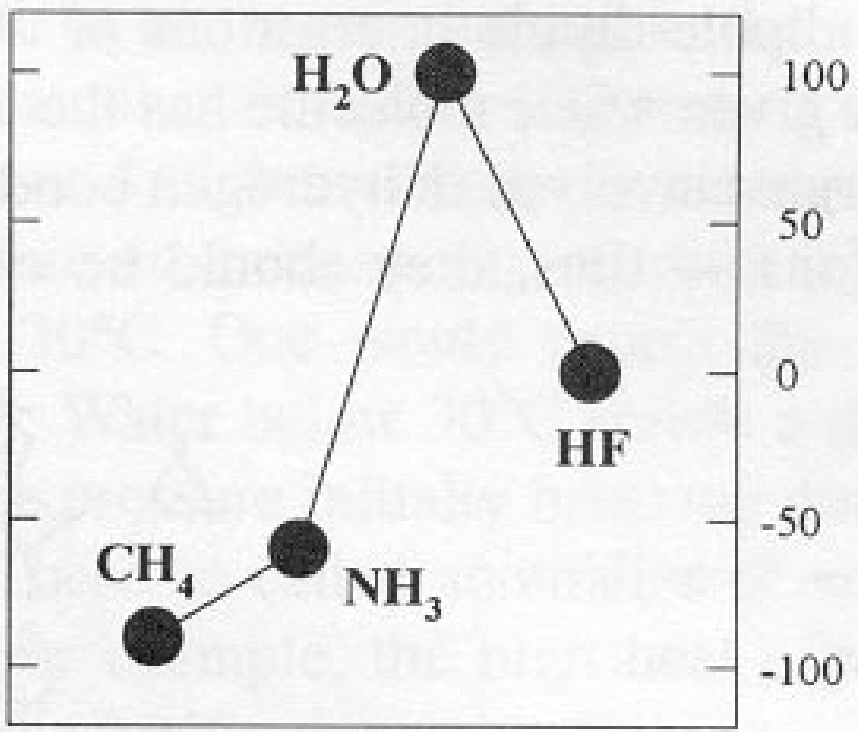
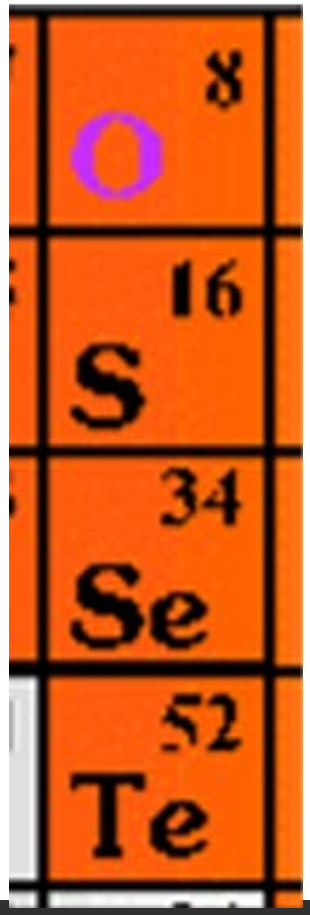


Figure 3.2 in Emerson & Hedges

FIGURE 4.1. Boiling points of compounds structurally similar to water.

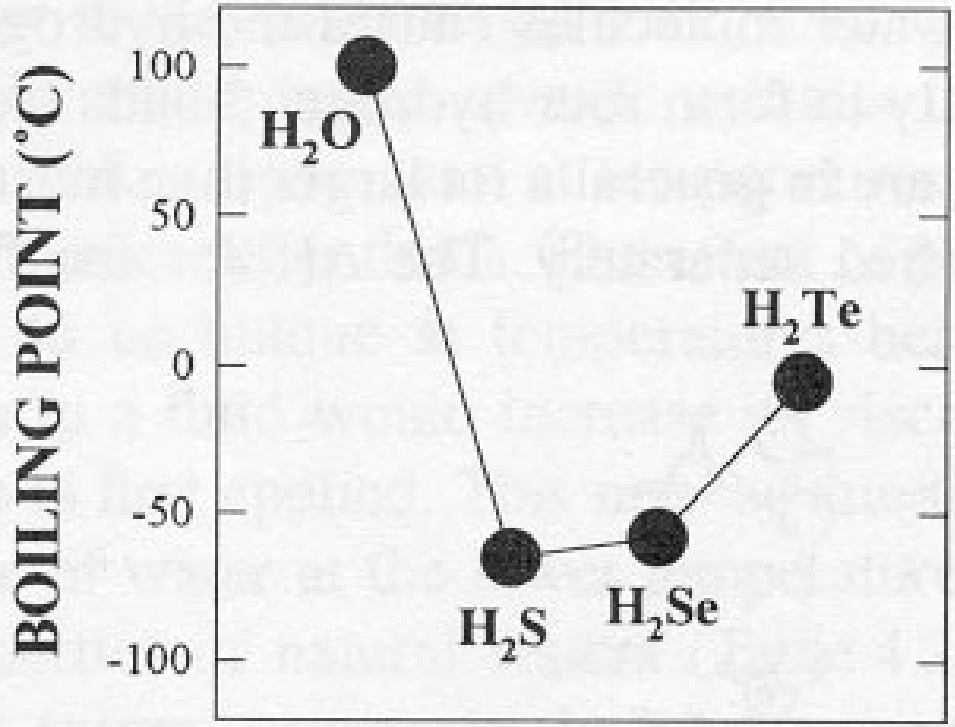
Look at O and its relatives



Outer shell electronic Configuration is the same

Group or Family 6A

Boiling Point Comparison



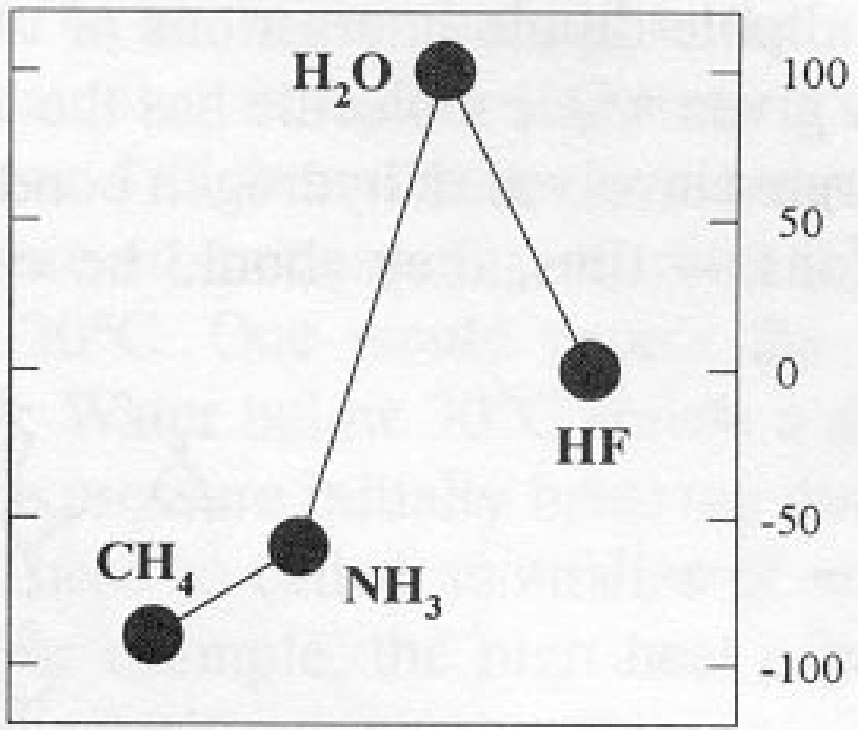
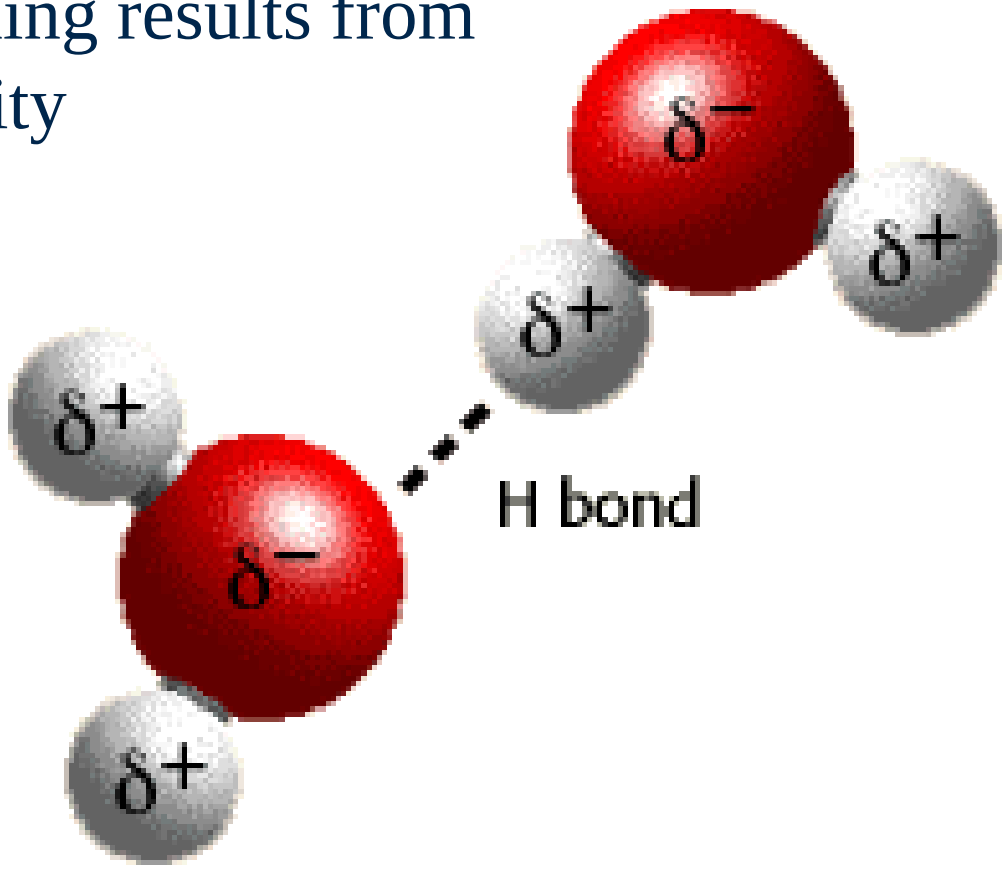


Figure 3.2 in Emerson & Hedges

FIGURE 4.1. Boiling points of compounds structurally similar to water.

Hydrogen Bonding is key to anomalous properties of water

H-Bonding results from polarity



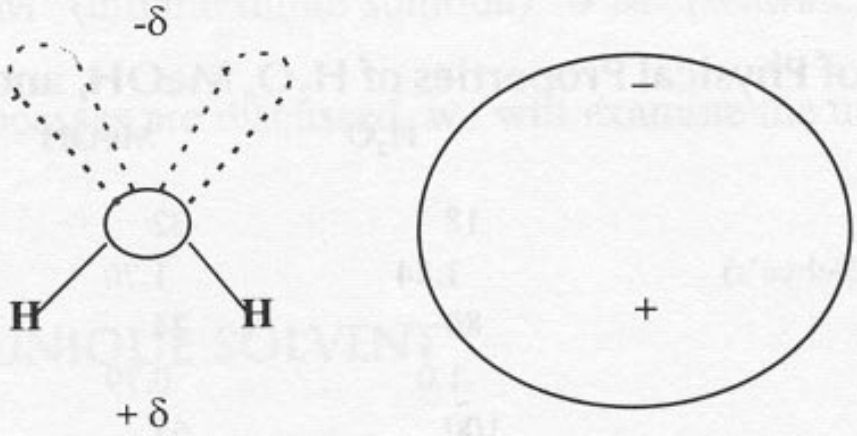


FIGURE 4.3. The water dipole.

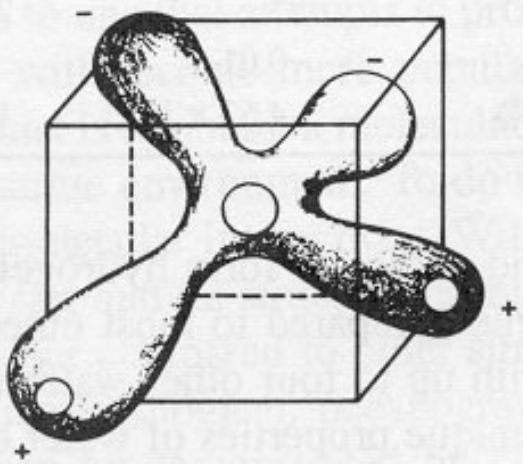
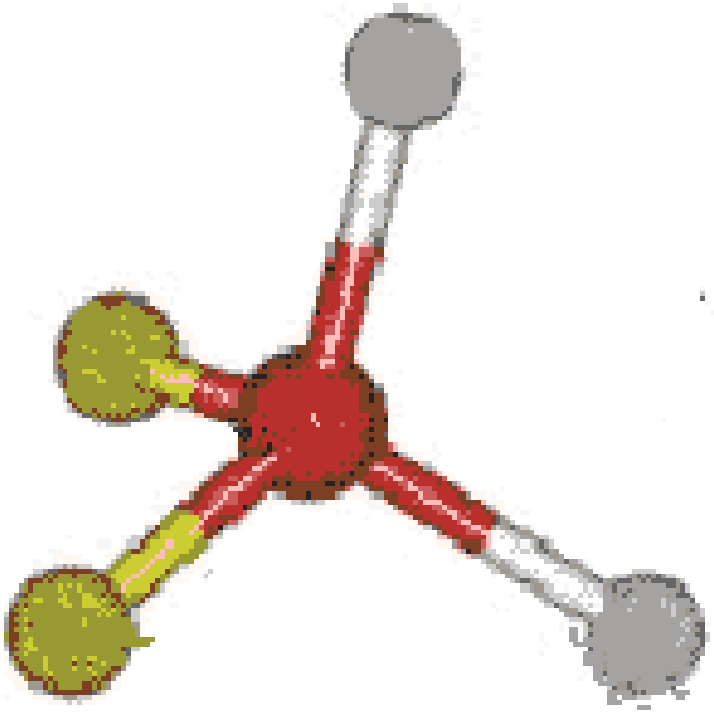


FIGURE 4.4. The three-dimensional structure of the water molecule.

Dipole & Quadrapole Diagrams

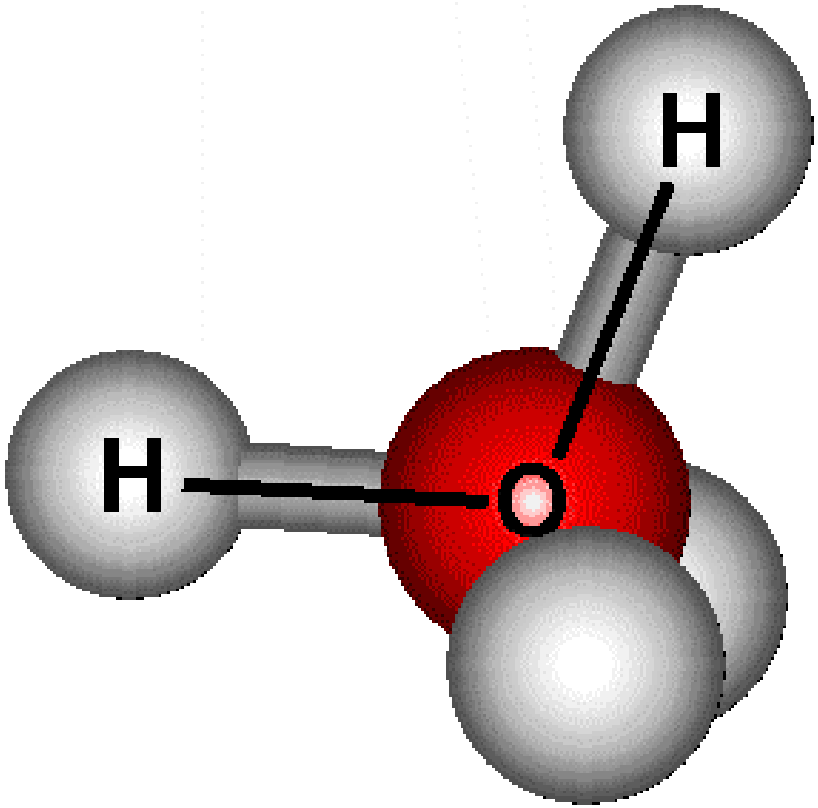
(Millero 2006) p. 125

Water dipole & quadrapole

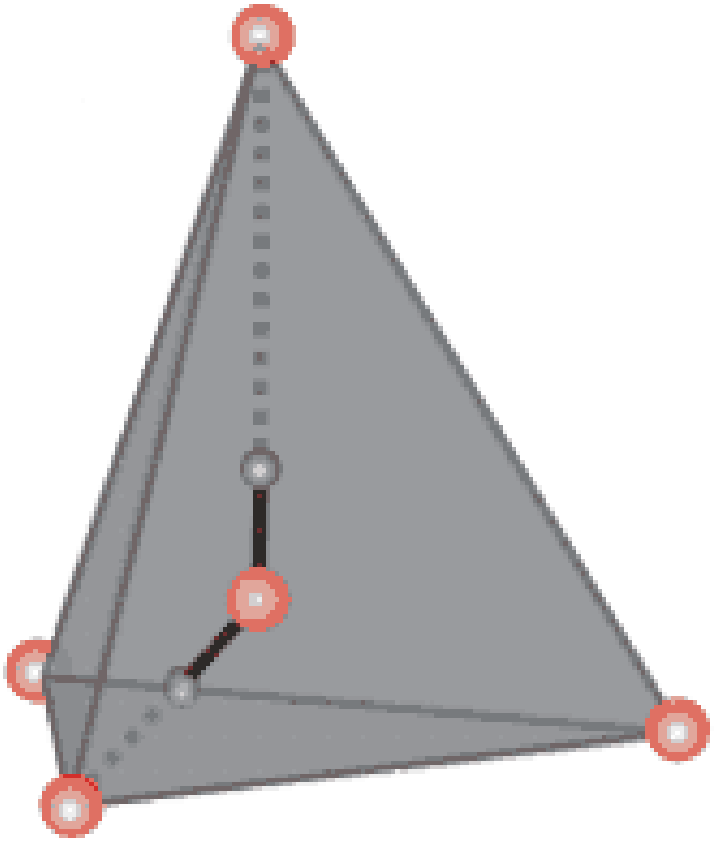


Oxygen is shown in red, Hydrogen is shown in gray & Electrons are depicted as yellow

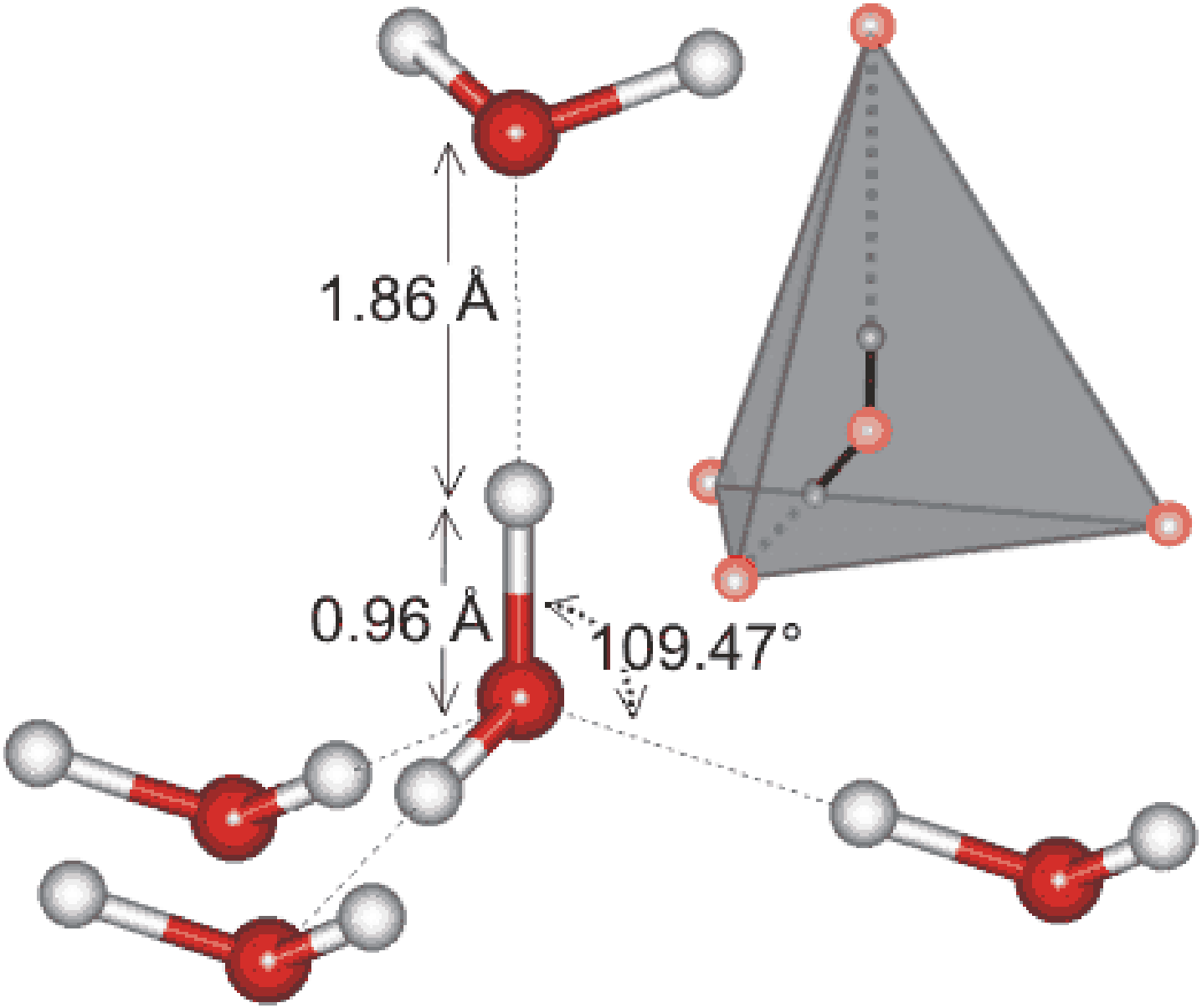
Yet another representation



Water Tetrahedron



The two non-bonded pairs of electrons on oxygen form the back two legs of the tetrahedron, but are not shown



Arrangement for Hydrogen Bonding - Pentamer

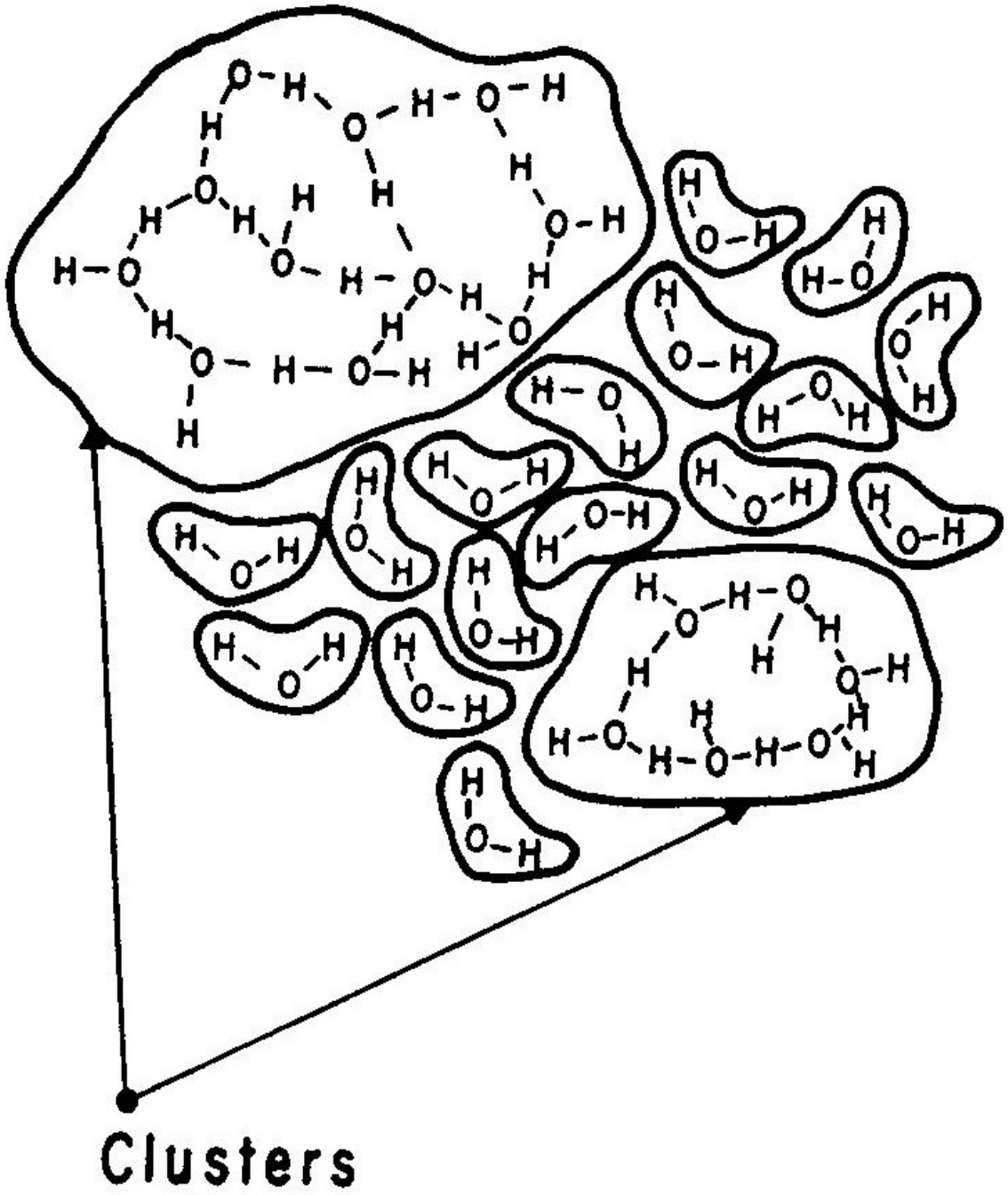
Hydrogen bonding in liquid water is always present

However, H-bonds are

constantly forming and breaking

It is a dynamic process that can be represented or modeled in several ways

See Millero (3rd ed) p 128–132 for models



Water Clusters Dynamically Form, Break and Re-form

Frank & Wen
Flickering Cluster Model

(Millero 2006)

Millero

TABLE 4.1
Comparison of Physical Properties of H_2O, MeOH, and n-Heptane

Property	H_2O	MeOH	n-Heptane
MW	18	32	100
Dipole moment (Debye's)	1.84	1.70	>0.2
Dielectric const.	80	24	1.97
Density (g cm^{-3})	1.0	0.79	0.73
B.P. (°C)	100	65	98.4
M.P. (°C)	0	–98	–97
Specific heat (cal g^{-1} deg^{-1})	1.0	0.56	0.5
ΔH_{vap} (cal g^{-1})	540	263	76
ΔH_{fus} (cal g^{-1})	79	22	34
Surface tension (dynes cm^{-1})	73	23	25
Viscosity 20°C (poise)	0.01	0.006	0.005
Compressibility 25°C (atm^{-1})	4.57×10^{-11}	12.2×10^{-11}	14×10^{-11}

Water Properties

High Heat Capacity (C_p)

(Heat energy to raise 1 g of water 1 ^oC)

Prevents extreme ranges of temperature (temp buffering)

Allows heat transfer by water masses to be large

Water Properties

High Heat of Fusion

($\Delta H = 79$ cal/g)

(Heat energy for melting solid)

Absorption or release of latent heat results in high thermostatic effect

a.k.a. Enthalpy of Fusion (kJ/kg)

Water Properties

High Heat of Vaporization

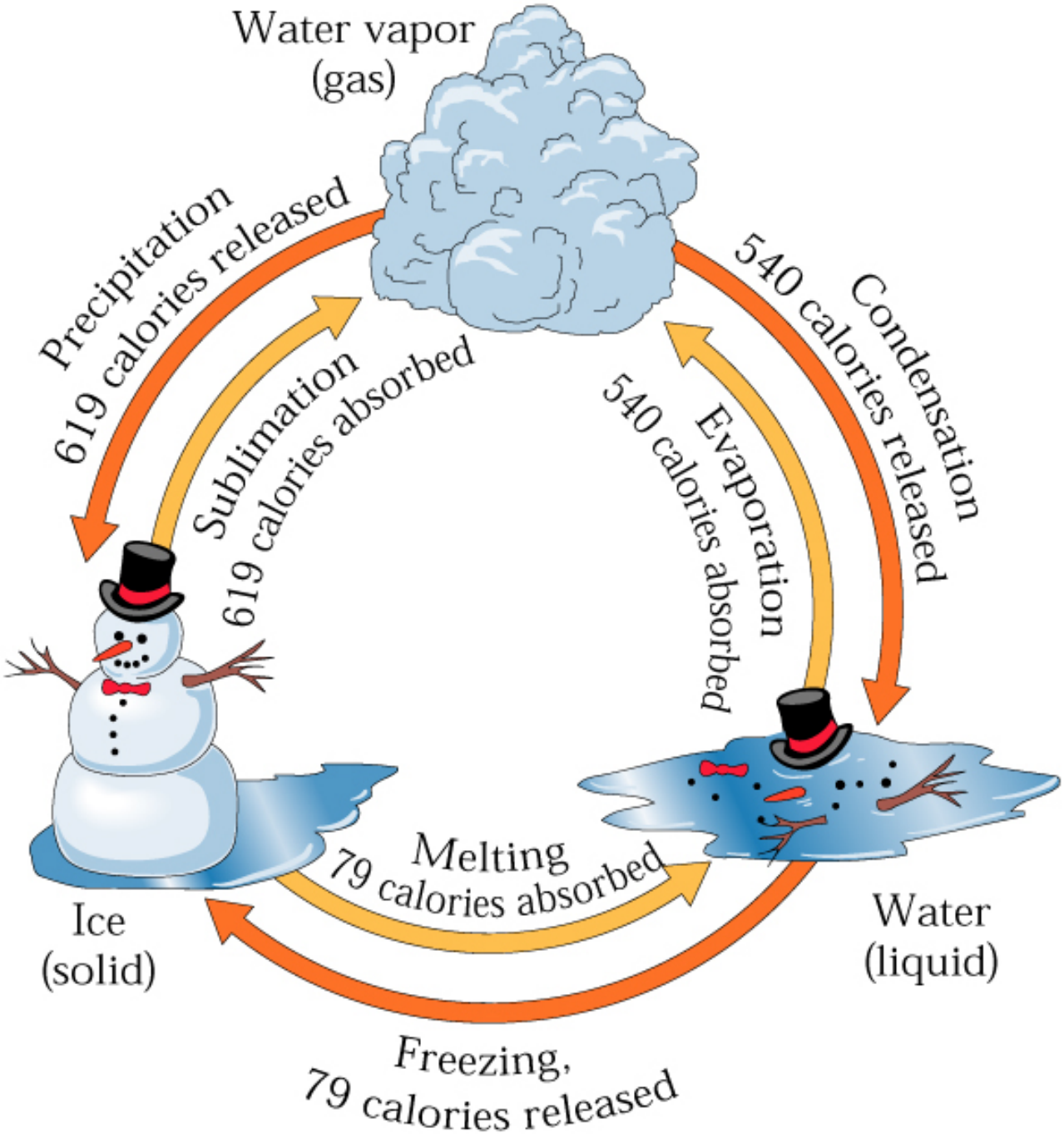
(ΔH = 540 cal/g)

(Heat energy for evaporating liquid)

Highest of all liquids

Results in evaporative cooling and transfer of heat to atmosphere, thermostating

a.k.a. Enthalpy of Vaporization



Large Quantities of Heat are Absorbed & Released During Phase Changes

(Wiley 1999)

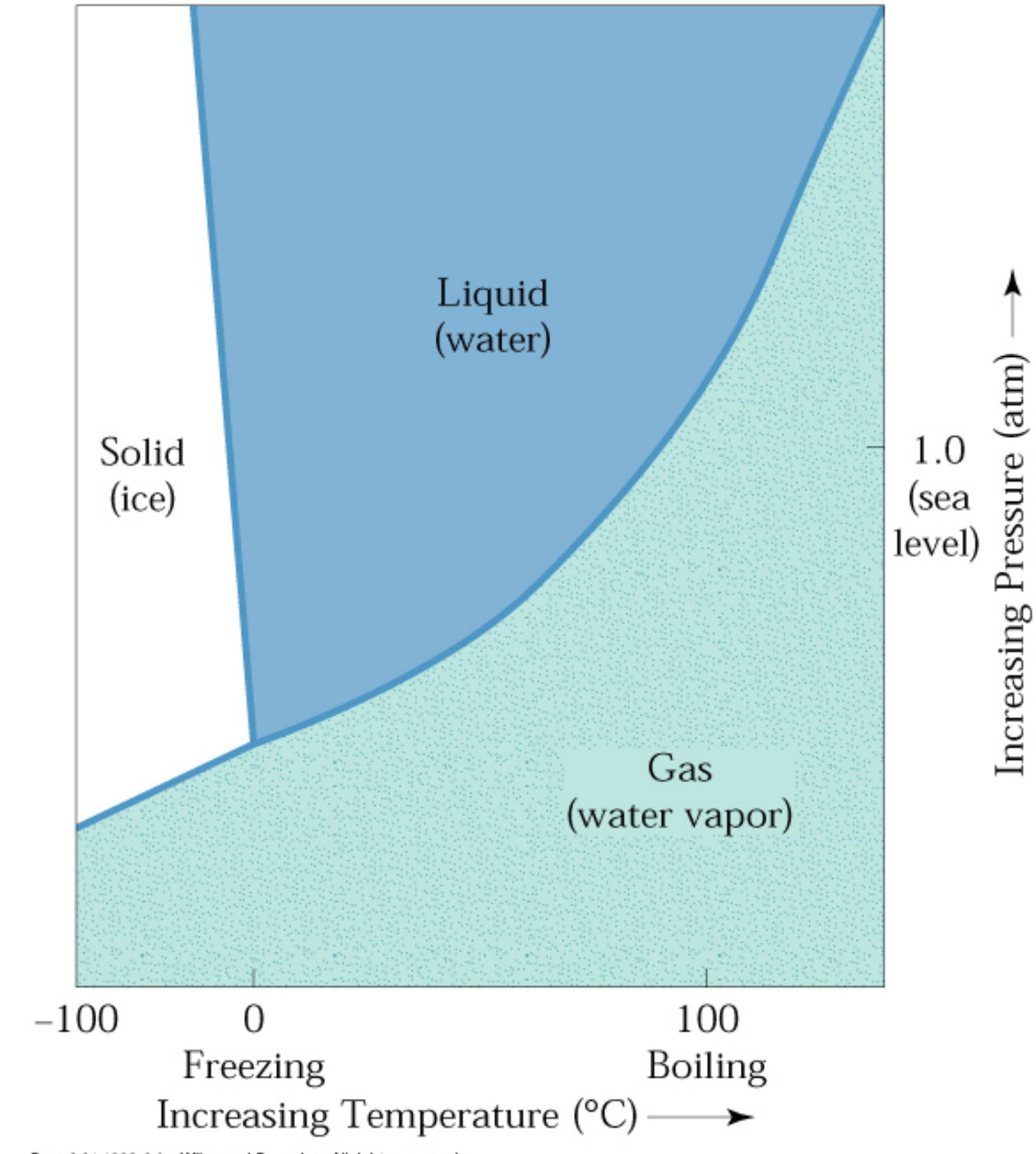
Water Properties

Thermal Expansion

(temperature of maximum density)

Waters with low or no salt content have maximum density above freezing points

Ice floats



Simple Phase Diagram of Water

(Wiley 1999)

Water Properties

High Dielectric Constant

(highest of almost all substances)

Results in charge insulating power

Important in dissolution of salts

Important in hydration of ions

Water Properties

Relatively High Viscosity

(high for low molecular weight substance)

Important in wave and current formation

Water Properties

High Surface Tension

(highest of all substances)

Controls drop formation, important in waves and many surface properties

Important in cell physiology

Interfacial Tension creates appearance of a “skin” on surface