

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: H₂O

- # 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

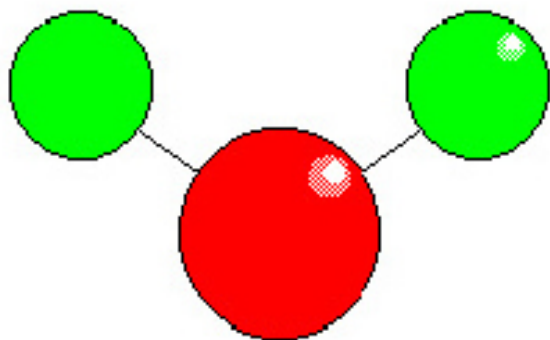


Chemical Oceanography

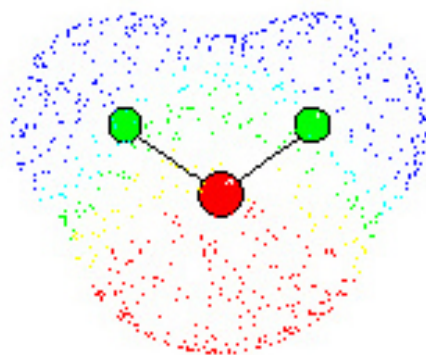
Physical Chemistry of Seawater (E&H Chap. 3)

- 💧 Seawater is 96.5 % H₂O
- 💧 Water unique substance & solvent
- 💧 Review structure
- 💧 Discuss selected unusual properties
- 💧 Consequences of water anomalies
- 💧 Phase diagrams

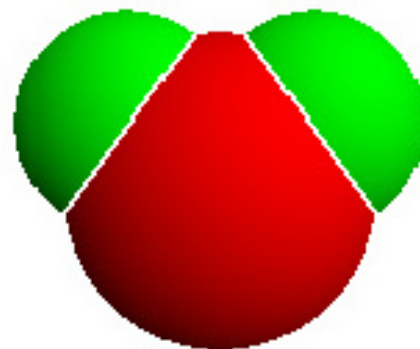
Molecular Structure of H₂O



"Ball & Stick"
Model



Electron
Density
Distribution



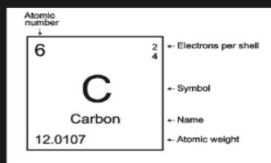
Space Filling
Model

Periodic Table of the Elements

Rows = Periods

Columns = Groups or Families

PERIODIC TABLE OF THE ELEMENTS



1 H HYDROGEN 1.0079																	2 He HELIUM 4.0026
3 Li LITHIUM 6.941	4 Be BERYLLIUM 9.0122											5 B BORON 10.811	6 C CARBON 12.011	7 N NITROGEN 14.007	8 O OXYGEN 15.999	9 F FLUORINE 18.998	10 Ne NEON 20.1797
11 Na SODIUM 22.989	12 Mg MAGNESIUM 24.305											13 Al ALUMINIUM 26.981	14 Si SILICON 28.085	15 P PHOSPHORUS 30.974	16 S SULFUR 32.066	17 Cl CHLORINE 35.453	18 Ar ARGON 39.948
19 K POTASSIUM 39.098	20 Ca CALCIUM 40.078	21 Sc SCANDIUM 44.955	22 Ti TITANIUM 47.867	23 V VANADIUM 50.9415	24 Cr CHROMIUM 51.9961	25 Mn MANGANESE 54.938	26 Fe IRON 55.845	27 Co COBALT 58.933	28 Ni NICKEL 58.6934	29 Cu COPPER 63.546	30 Zn ZINC 65.38	31 Ga GALLIUM 69.723	32 Ge GERMANIUM 72.63	33 As ARSENIC 74.921	34 Se SELENIUM 78.971	35 Br BROMINE 79.904	36 Kr KRYPTON 83.798
37 Rb RUBIDIUM 85.467	38 Sr STRONTIUM 87.62	39 Y YTTRIUM 88.905	40 Zr ZIRCONIUM 91.224	41 Nb NIOBIUM 92.9063	42 Mo MOLYBDENUM 95.95	43 Tc TECHNETIUM (98)	44 Ru RUTHENIUM 101.07	45 Rh RHODIUM 102.90	46 Pd PALLADIUM 106.42	47 Ag SILVER 107.8682	48 Cd CADMIUM 112.414	49 In INDIUM 114.818	50 Sn TIN 118.710	51 Sb ANTIMONY 121.760	52 Te TELLURIUM 127.60	53 I IODINE 126.90	54 Xe XENON 131.293
55 Cs CAESIUM 132.905	56 Ba BARIUM 137.327	57-71*	72 Hf HAFNIUM 178.49	73 Ta TANTALUM 180.94	74 W TUNGSTEN 183.84	75 Re RHENIUM 186.207	76 Os OSMIUM 192.227	77 Ir IRIDIUM 192.222	78 Pt PLATINUM 195.084	79 Au GOLD 196.96657	80 Hg MERCURY 200.59	81 Tl THALLIUM 204.38	82 Pb LEAD 207.2	83 Bi BISMUTH 208.9804	84 Po POLONIUM (209)	85 At ASTATINE (210)	86 Rn RADON (222)
87 Fr FRANCIUM (223)	88 Ra RADIUM (226)	89-103**	104 Rf RUTHERFORDIUM (261)	105 Db DUBNIUM (268)	106 Sg SEABORGIUM (271)	107 Bh BOHRIUM (272)	108 Hs HASSIUM (277)	109 Mt MEITNERIUM (276)	110 Ds DARMSTADTIUM (281)	111 Rg ROENTGIENIUM (280)	112 Cn COPERNICIUM (285)	113 Nh NIHOIUM (286)	114 Fl FLEROVIUM (289)	115 Mc MOSCOWIUM (289)	116 Lv LIVERMORIUM (293)	117 Ts TENNESSINE (294)	118 Og OGANESSON (294)
		57 La LANTHANUM 138.90	58 Ce CERIUM 140.118	59 Pr PRASEODYMIUM 140.90	60 Nd NEODYMIUM 144.242	61 Pm PROMETHIUM (145)	62 Sm SAMARIUM 150.36	63 Eu EUROPIUM 151.964	64 Gd GADOLINIUM 157.25	65 Tb TERBIUM 158.92	66 Dy DYSPROSIUM 162.590	67 Ho HOLMIUM 164.93	68 Er ERBIUM 167.259	69 Tm THULIUM 168.93	70 Yb YTTERIUM 173.054	71 Lu LUTETIUM 174.967	
		89 Ac ACTINIUM (227)	90 Th THORIUM 232.0377	91 Pa PROTACTINIUM 231.03	92 U URANIUM 238.02	93 Np NEPTUNIUM (237)	94 Pu PLUTONIUM (244)	95 Am AMERICIUM (243)	96 Cm CURIUM (247)	97 Bk BERKELIUM (247)	98 Cf CALIFORNIUM (251)	99 Es EINSTEINIUM (252)	100 Fm FERMIUM (257)	101 Md MENDELEVIUM (258)	102 No NOBELIUM (259)	103 Lr LAWRENCIUM (262)	

- Non-metal
- Alkali metal
- Alkaline earth metal
- Transition metal
- Metal
- Metalloid
- Halogen
- Noble gas
- Lanthanide
- Actinide

Zoom in on O and its neighbors

Part of one period

C ⁶	N ⁷	O ⁸	F ⁹
----------------	----------------	----------------	----------------

Each can form compounds
with hydrogen

Boiling Point Comparison

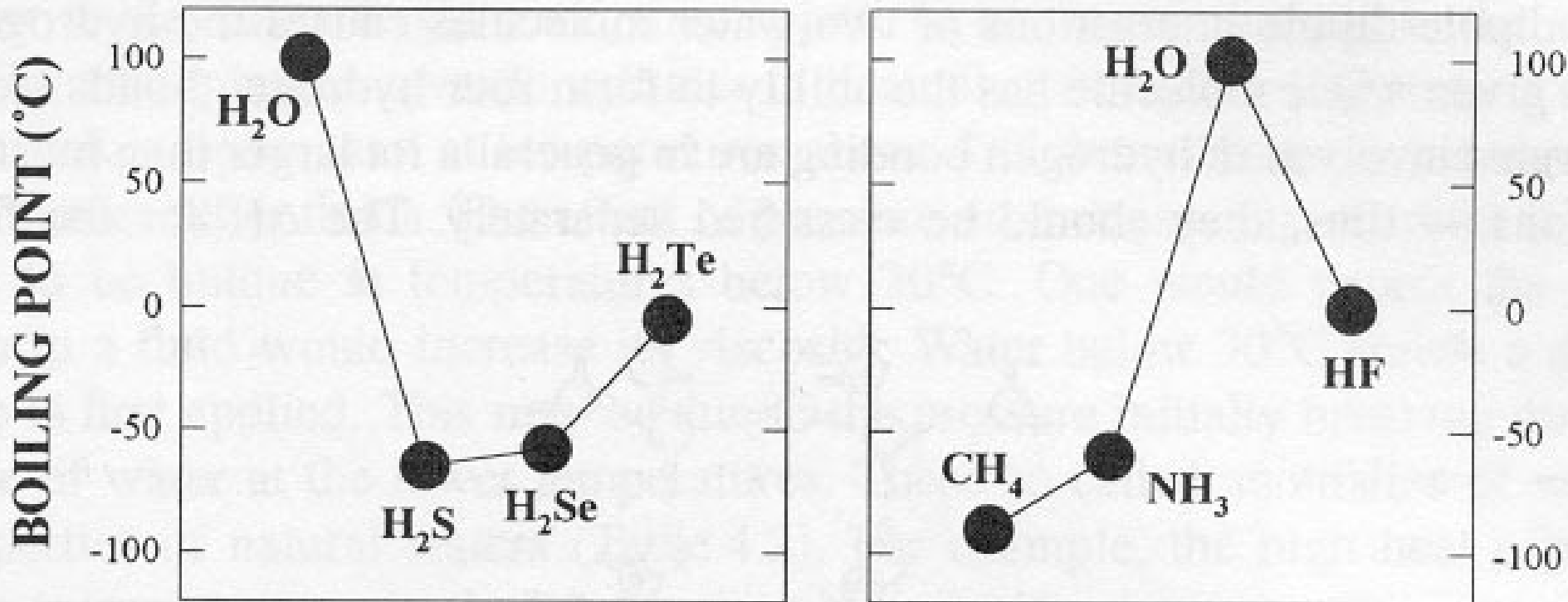


Figure 3.2 in Emerson & Hedges

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

Look at O and its relatives

	8
O	
	16
S	
	34
Se	
	52
Te	

Outer shell electronic
Configuration is the same

Group or Family 6A

Boiling Point Comparison

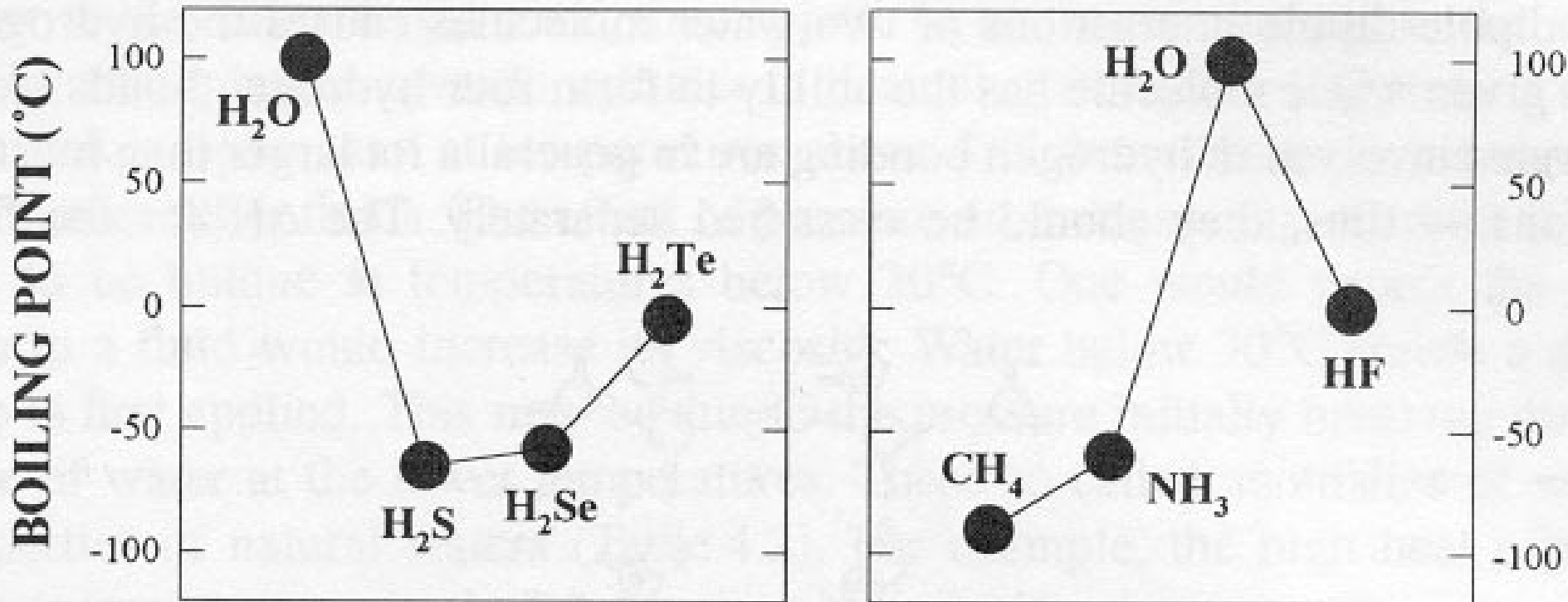
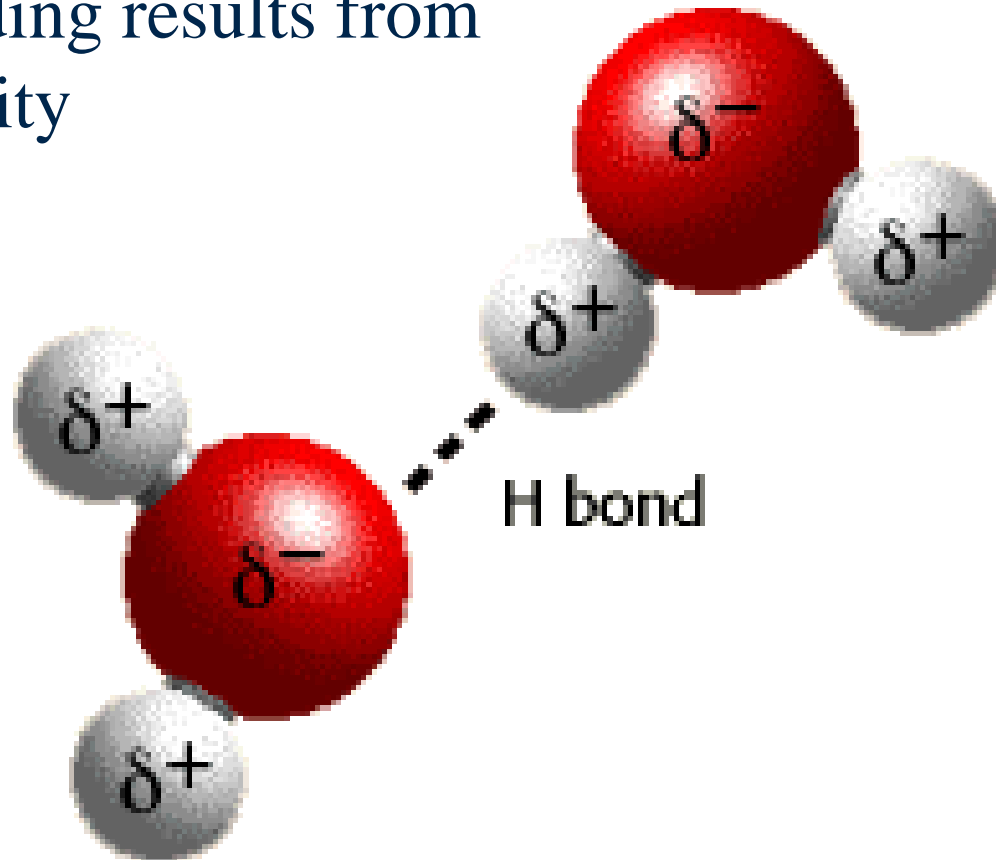


Figure 3.2 in Emerson & Hedges

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



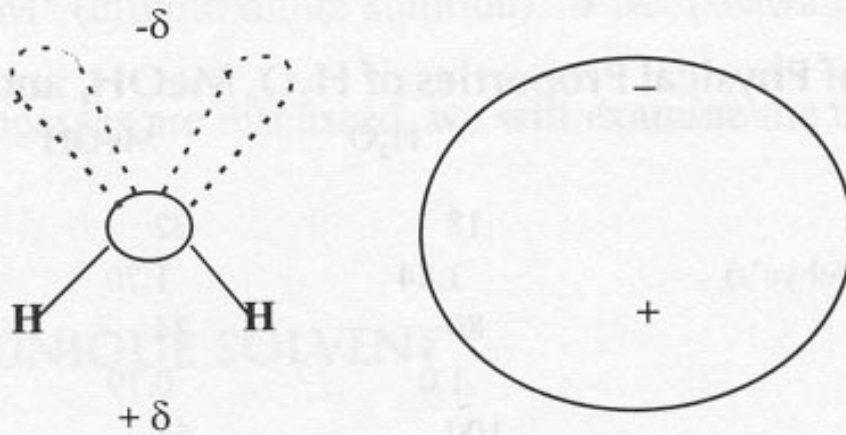


FIGURE 4.3. The water dipole.

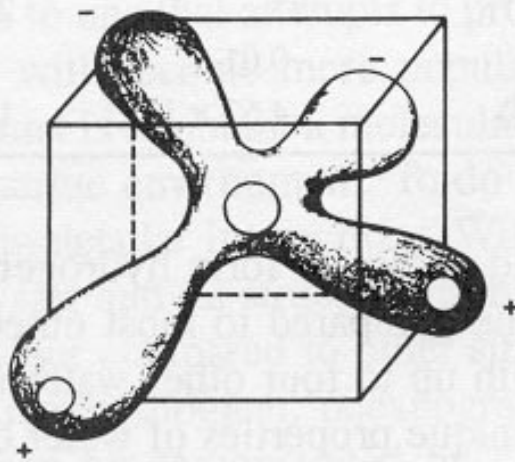
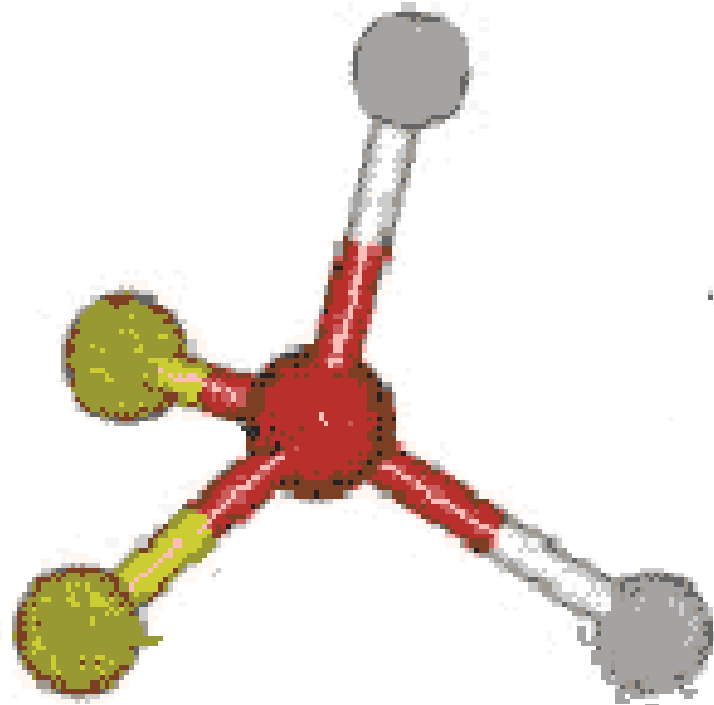


FIGURE 4.4. The three-dimensional structure of the water molecule.

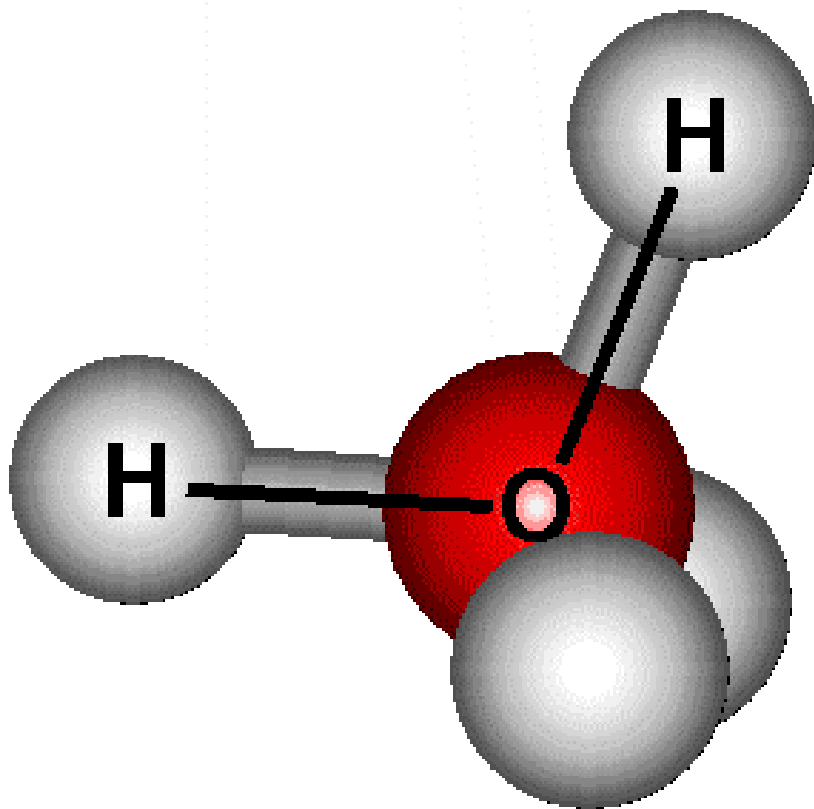
Dipole &
 Quadrupole
 Diagrams
 (Millero 2006)
 p. 125

Water dipole & quadrupole

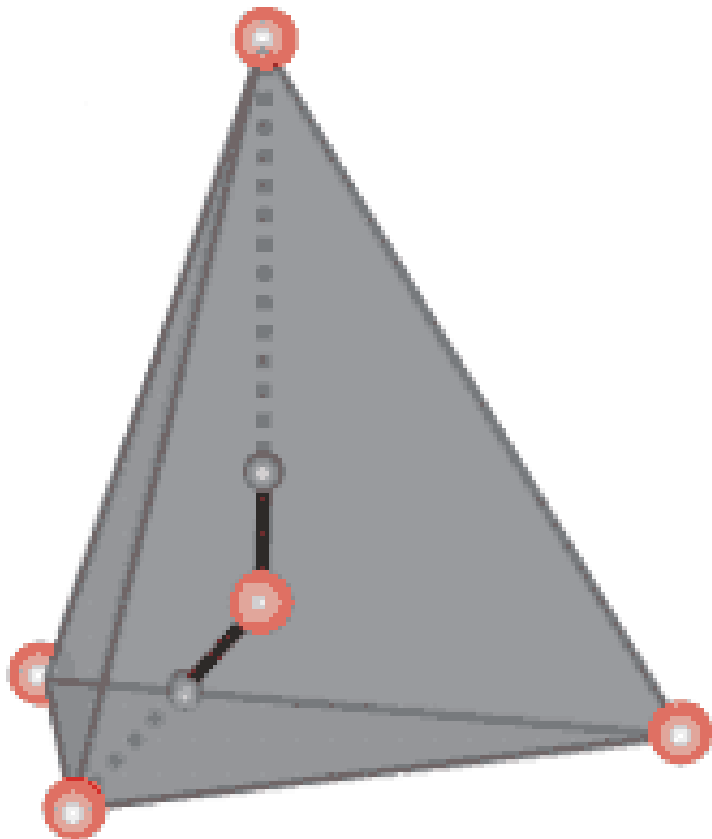


Oxygen is shown in red, Hydrogen is shown in gray & Electrons are depicted as yellow

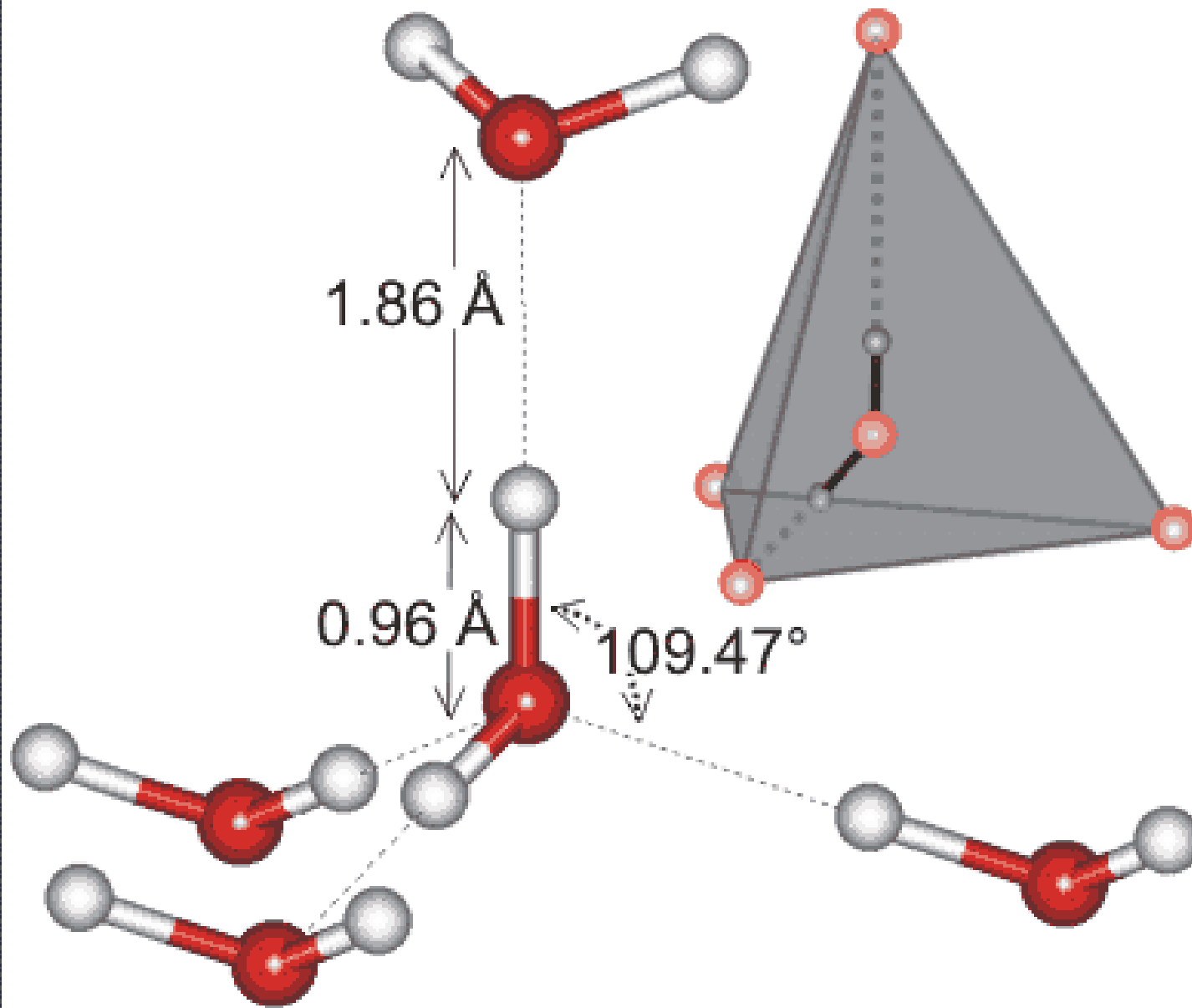
Yet another representation



Water Tetrahedron



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

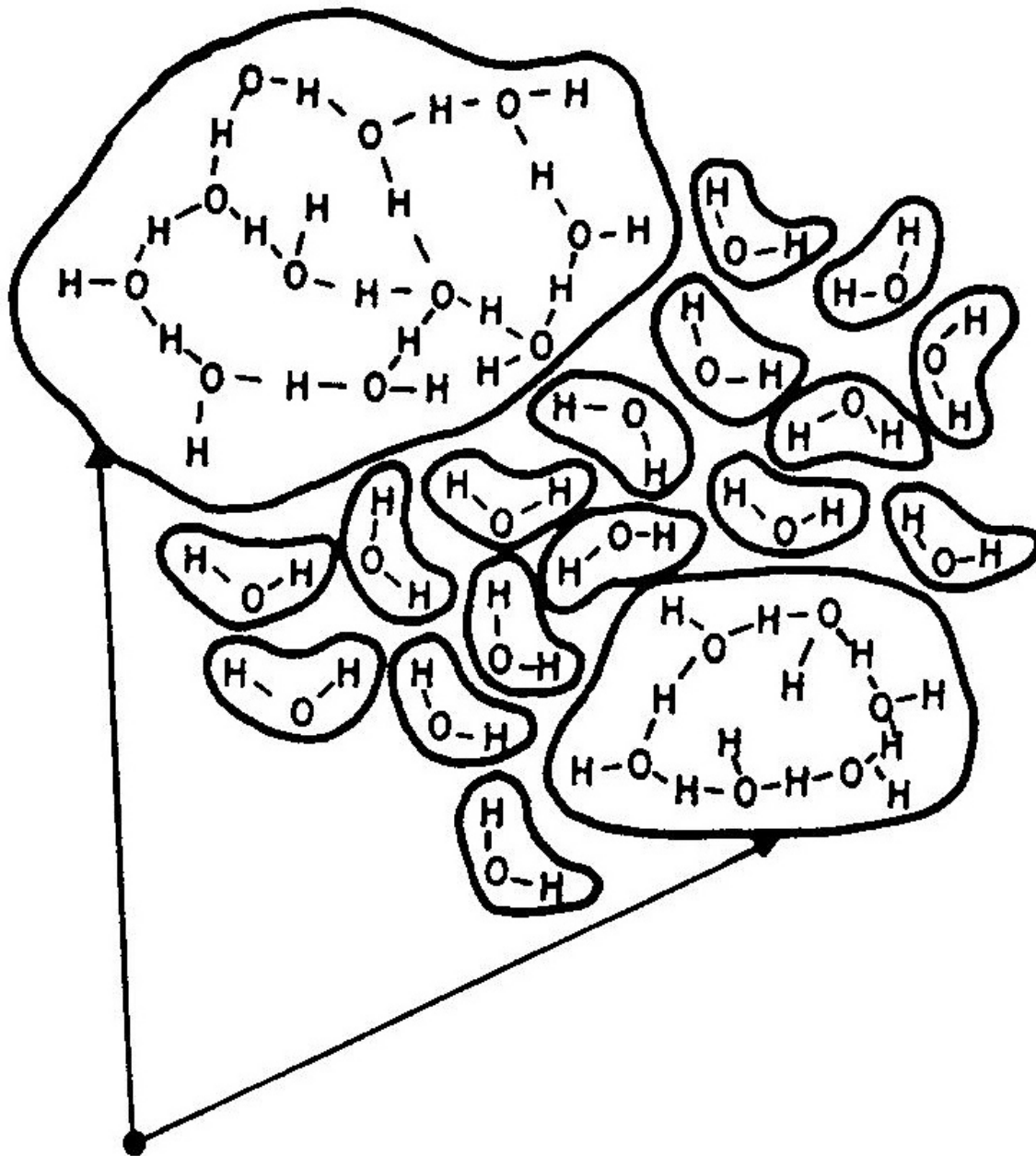


Hydrogen bonding
in liquid water is
always present

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

19

(Millero 2006)

Millero

TABLE 4.1

Comparison of Physical Properties of H₂O, MeOH, and n-Heptane

Property	H ₂ O	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 °C)

Prevents extreme ranges of temperature (temp buffering)

Allows heat transfer by water masses to be large

Water Properties

High Heat of Fusion

($\Delta H = 79 \text{ cal/g}$)

(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

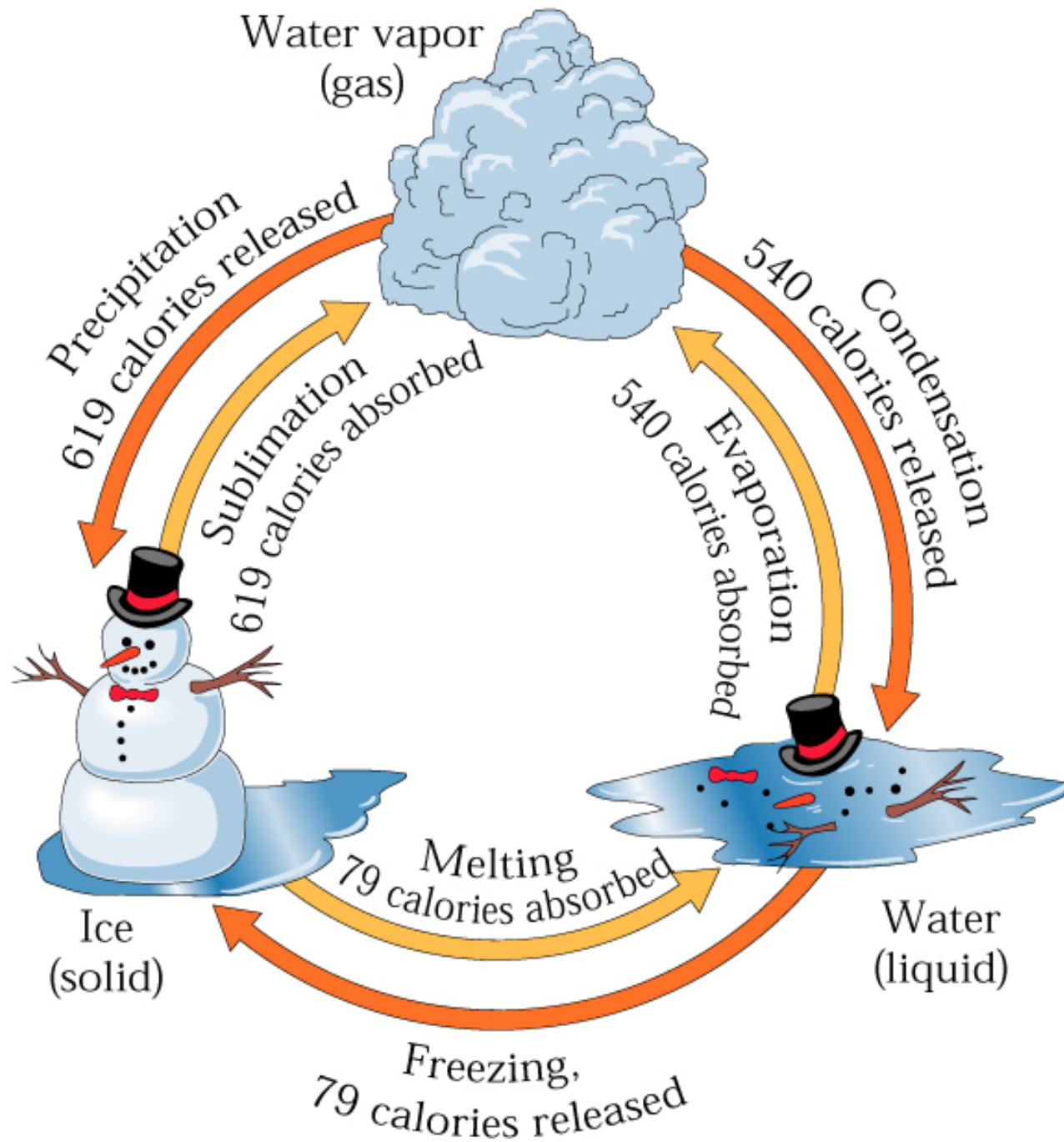
High Heat of Vaporization
($\Delta H = 540 \text{ cal/g}$)

(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

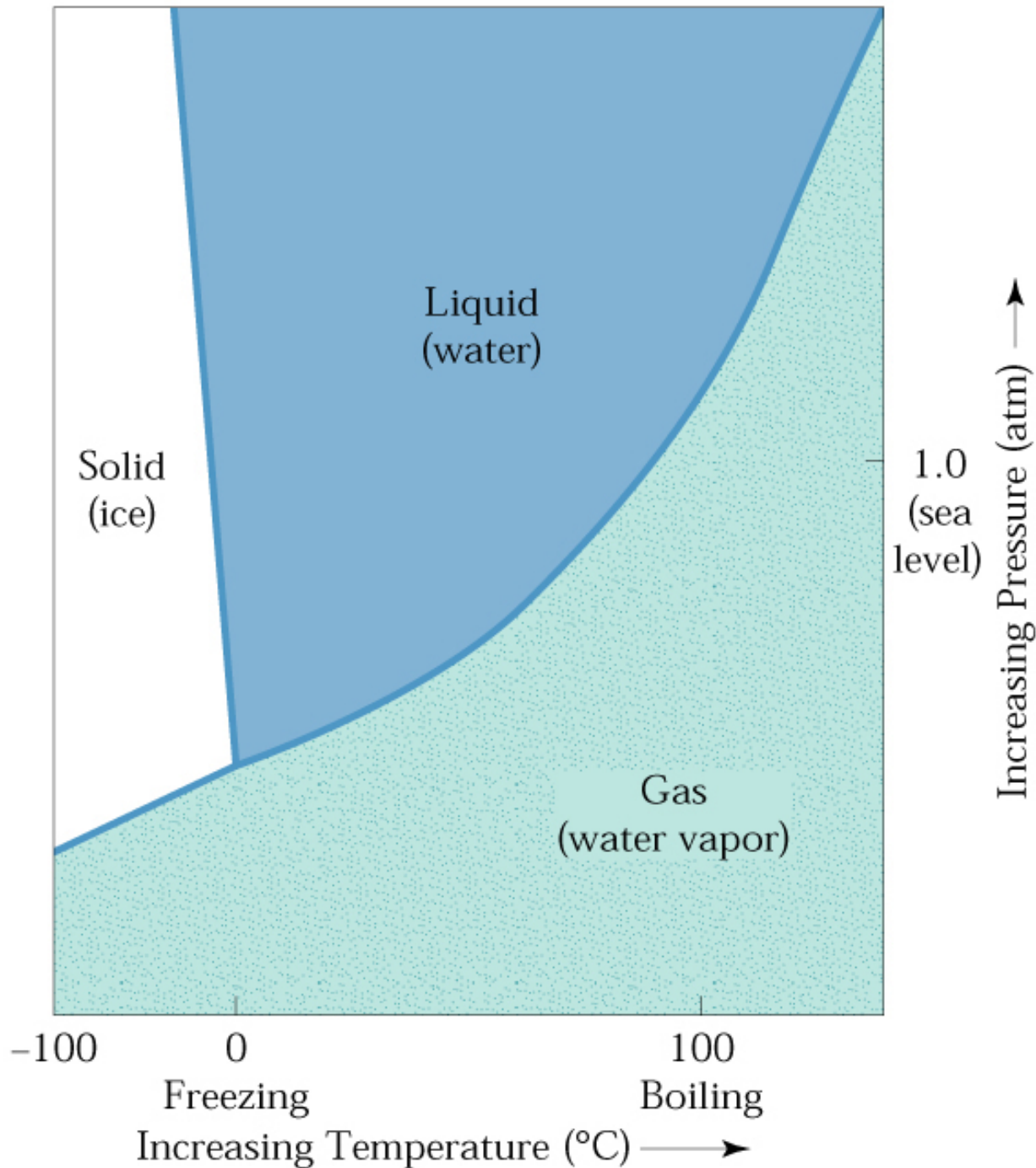
Water Properties

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

