

Chemical Oceanography



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Username: chemocean

Password: letmein

Websites of interest Re: H₂O

- # www.biology.arizona.edu/biochemistry/tutorials/chemistry/page3.html
- # www.science.uwaterloo.ca/~cchieh/cact/applychem/waterchem.html
- # www.biologie.uni-hamburg.de/b-online/e18/18c.htm

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

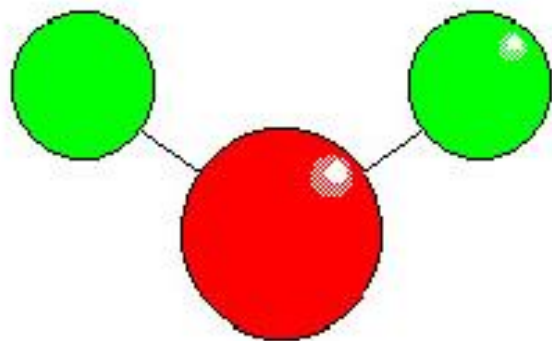


Chemical Oceanography

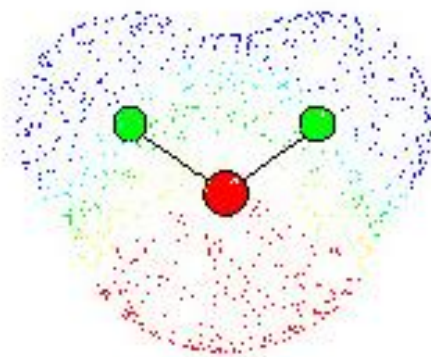
Physical Chemistry of Seawater (E&H Chap. 3)

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

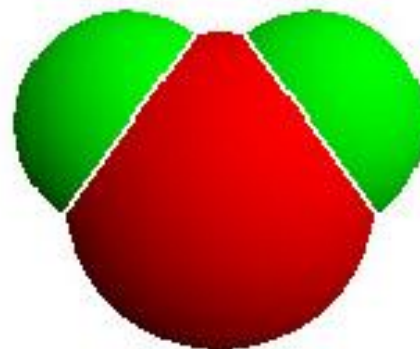
Molecular Structure of H₂O



**“Ball & Stick”
Model**



**Electron
Density
Distribution**



**Space Filling
Model**

Periodic Table of the Elements

Rows = Periods

Columns = Groups or Families

| | | | | | | | | | | | | | | | | | | | | |
|-------------------------|-------------------------|-------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|---------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--|--|------------------------|
| H ¹ | | | | | | | | | | | | | | | | | | | | He ² |
| Li ³ | Be ⁴ | | | | | | | | | | | B ⁵ | C ⁶ | N ⁷ | O ⁸ | F ⁹ | Ne ¹⁰ | | | |
| Na ¹¹ | Mg ¹² | | | | | | | | | | | Al ¹³ | Si ¹⁴ | P ¹⁵ | S ¹⁶ | Cl ¹⁷ | Ar ¹⁸ | | | |
| K ¹⁹ | Ca ²⁰ | Sc ²¹ | Ti ²² | V ²³ | Cr ²⁴ | Mn ²⁵ | Fe ²⁶ | Co ²⁷ | Ni ²⁸ | Cu ²⁹ | Zn ³⁰ | Ga ³¹ | Ge ³² | As ³³ | Se ³⁴ | Br ³⁵ | Kr ³⁶ | | | |
| Rb ³⁷ | Sr ³⁸ | Y ³⁹ | Zr ⁴⁰ | Nb ⁴¹ | Mo ⁴² | Tc ⁴³ | Ru ⁴⁴ | Rh ⁴⁵ | Pd ⁴⁶ | Ag ⁴⁷ | Cd ⁴⁸ | In ⁴⁹ | Sn ⁵⁰ | Sb ⁵¹ | Te ⁵² | I ⁵³ | Xe ⁵⁴ | | | |
| Cs ⁵⁵ | Ba ⁵⁶ | La ⁵⁷ | Hf ⁷² | Ta ⁷³ | W ⁷⁴ | Re ⁷⁵ | Os ⁷⁶ | Ir ⁷⁷ | Pt ⁷⁸ | Au ⁷⁹ | Hg ⁸⁰ | Tl ⁸¹ | Pb ⁸² | Bi ⁸³ | Po ⁸⁴ | At ⁸⁵ | Rn ⁸⁶ | | | |
| Fr ⁸⁷ | Ra ⁸⁸ | Ac ⁸⁹ | Rf ¹⁰⁴ | Db ¹⁰⁵ | Sg ¹⁰⁶ | Bh ¹⁰⁷ | Hs ¹⁰⁸ | Mt ¹⁰⁹ | Uun ¹¹⁰ | | | | | | | | | | | |

| | | | | | | | | | | | | | |
|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Ce ⁵⁸ | Pr ⁵⁹ | Nd ⁶⁰ | Pm ⁶¹ | Sm ⁶² | Eu ⁶³ | Gd ⁶⁴ | Tb ⁶⁵ | Dy ⁶⁶ | Ho ⁶⁷ | Er ⁶⁸ | Tm ⁶⁹ | Yb ⁷⁰ | Lu ⁷¹ |
| Th ⁹⁰ | Pa ⁹¹ | U ⁹² | Np ⁹³ | Pu ⁹⁴ | Am ⁹⁵ | Cm ⁹⁶ | Bk ⁹⁷ | Cf ⁹⁸ | Es ⁹⁹ | Fm ¹⁰⁰ | Md ¹⁰¹ | No ¹⁰² | Lr ¹⁰³ |

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

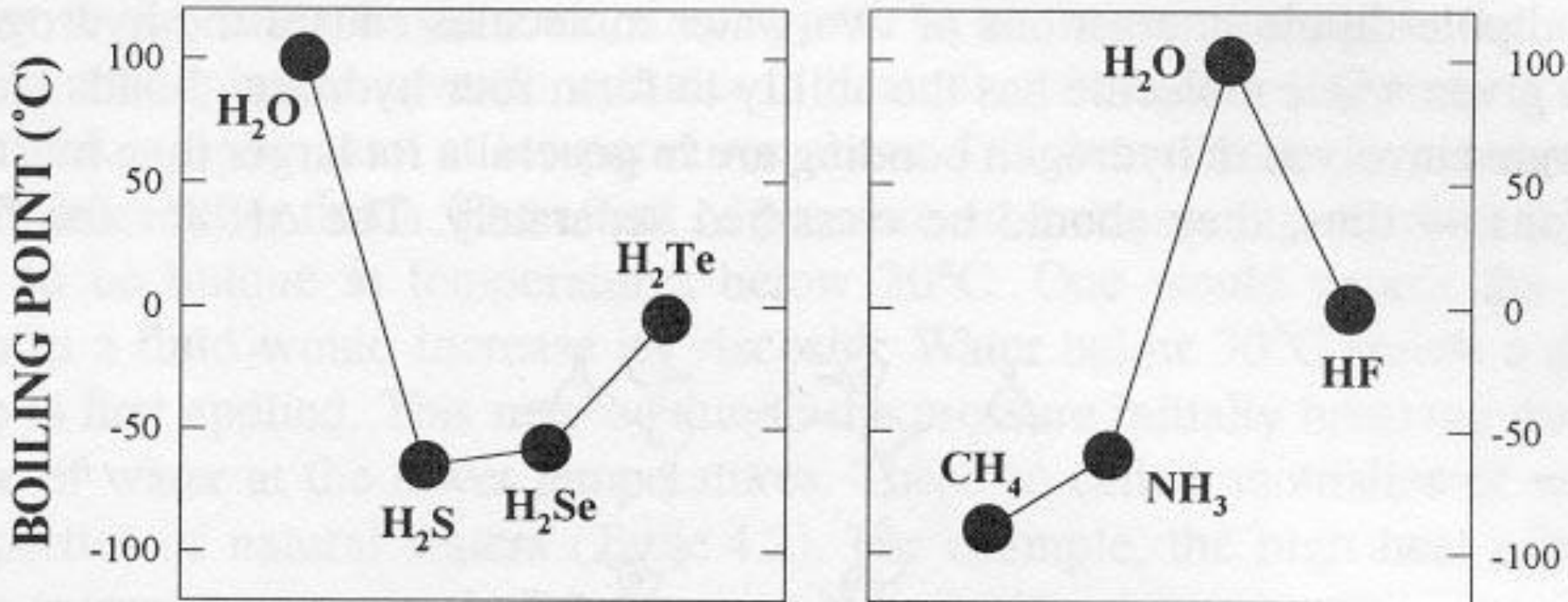


Figure 3.2 in Emerson & Hedges

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

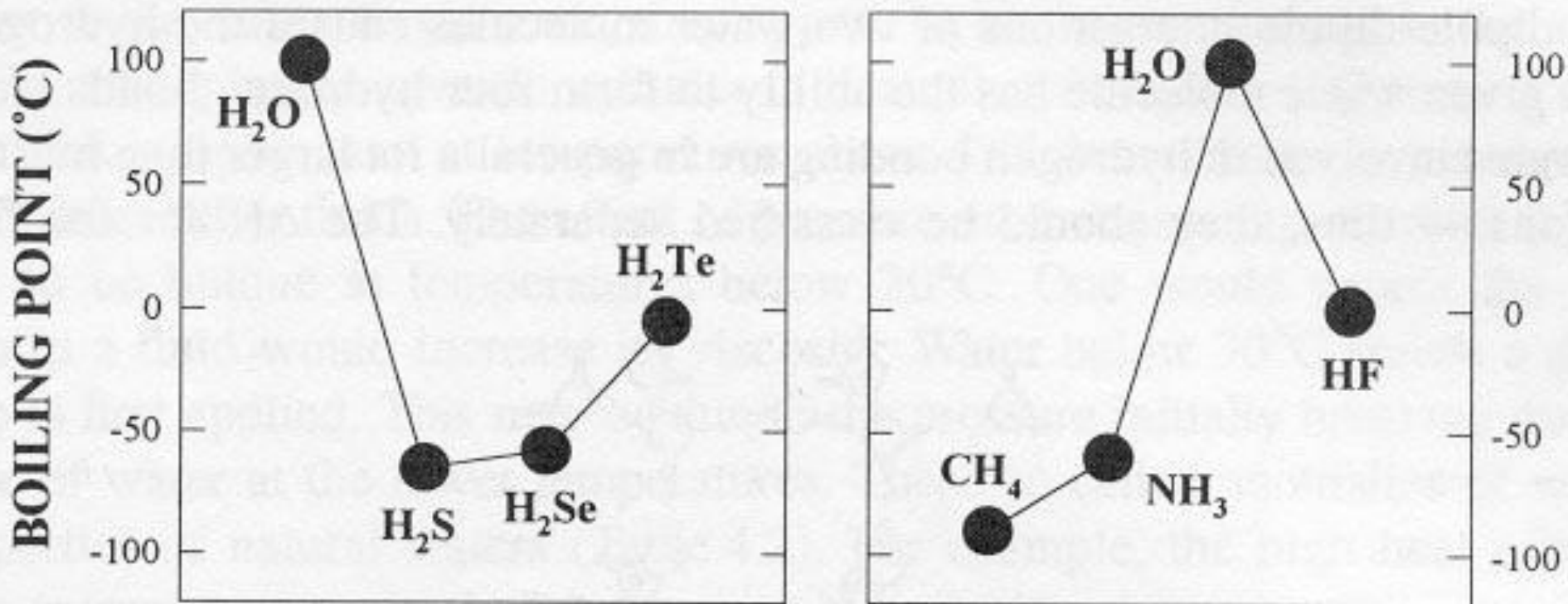
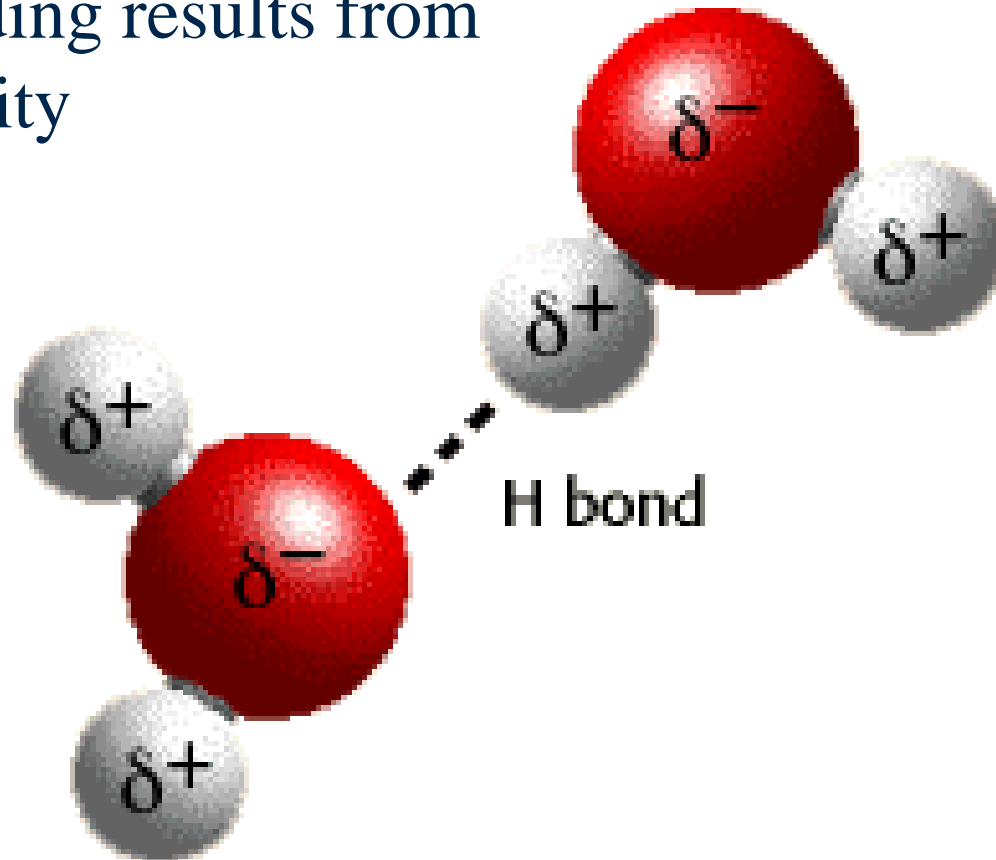


Figure 3.2 in Emerson & Hedges

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



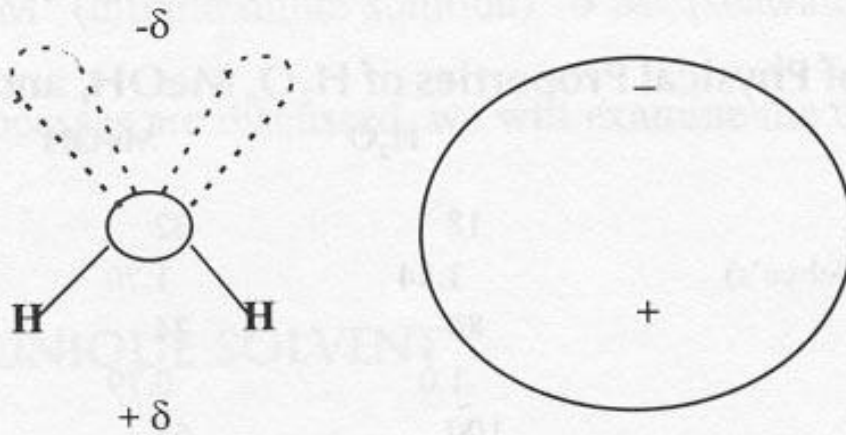


FIGURE 4.3. The water dipole.

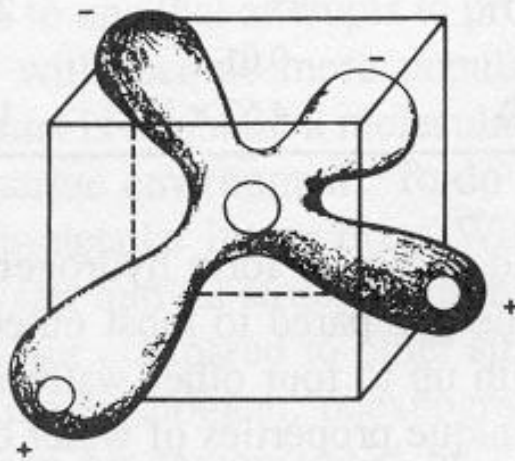
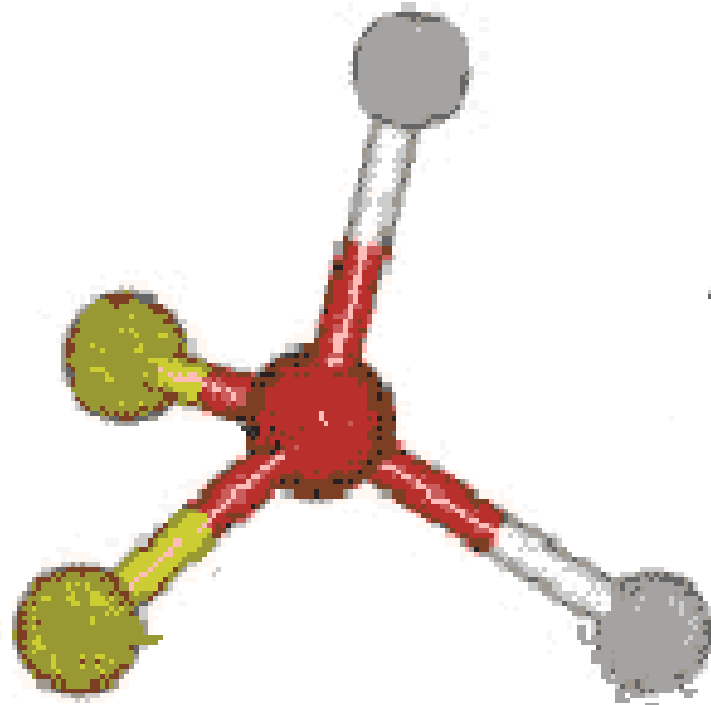


FIGURE 4.4. The three-dimensional structure of the water molecule.

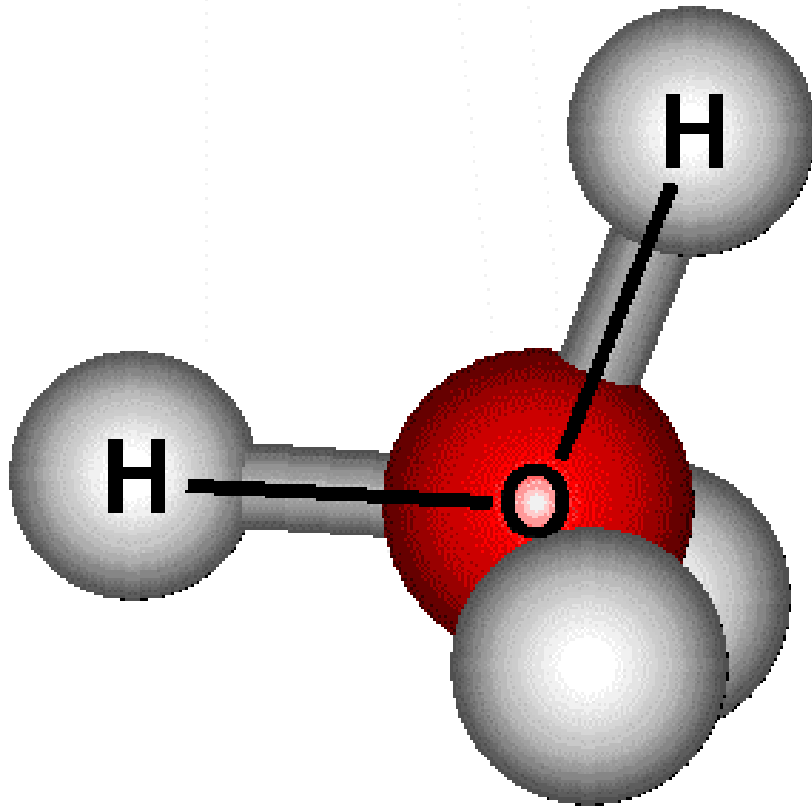
**Dipole &
Quadrupole
Diagrams
(Millero 2006)
p. 125**

Water dipole & quadrupole

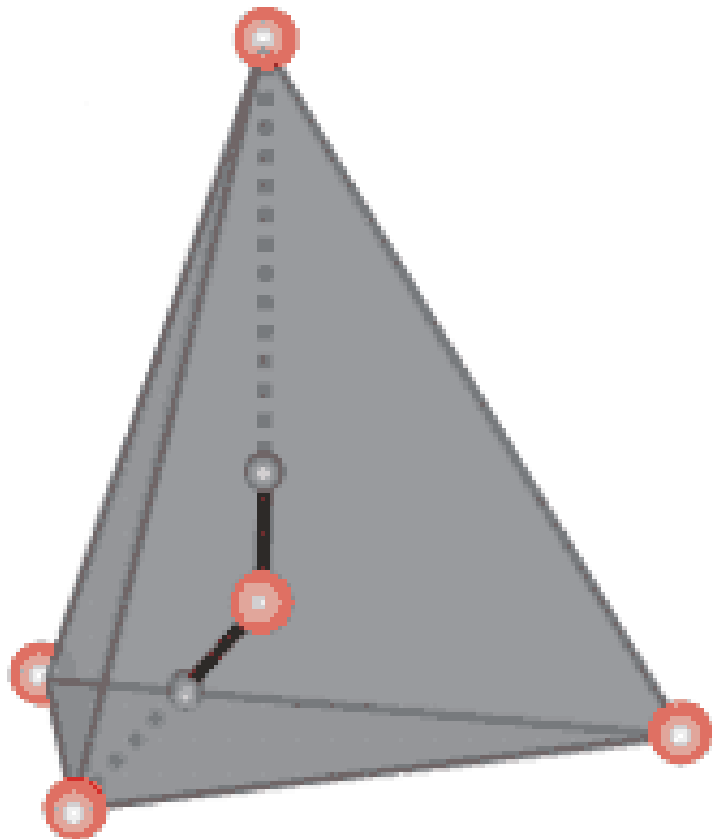


Oxygen is shown in red, Hydrogen is shown in gray & Electrons are depicted as yellow

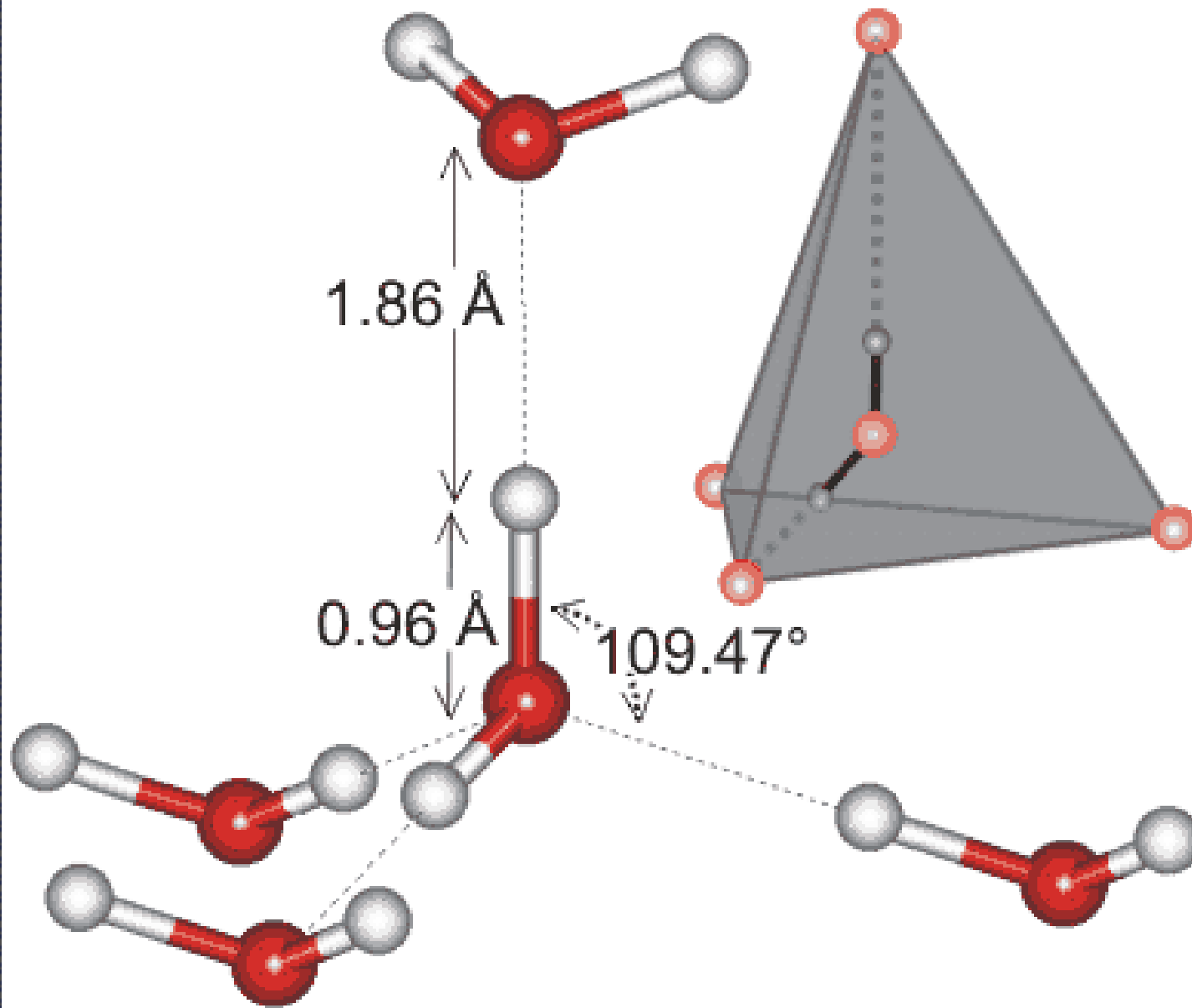
Yet another representation



Water Tetrahedron



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

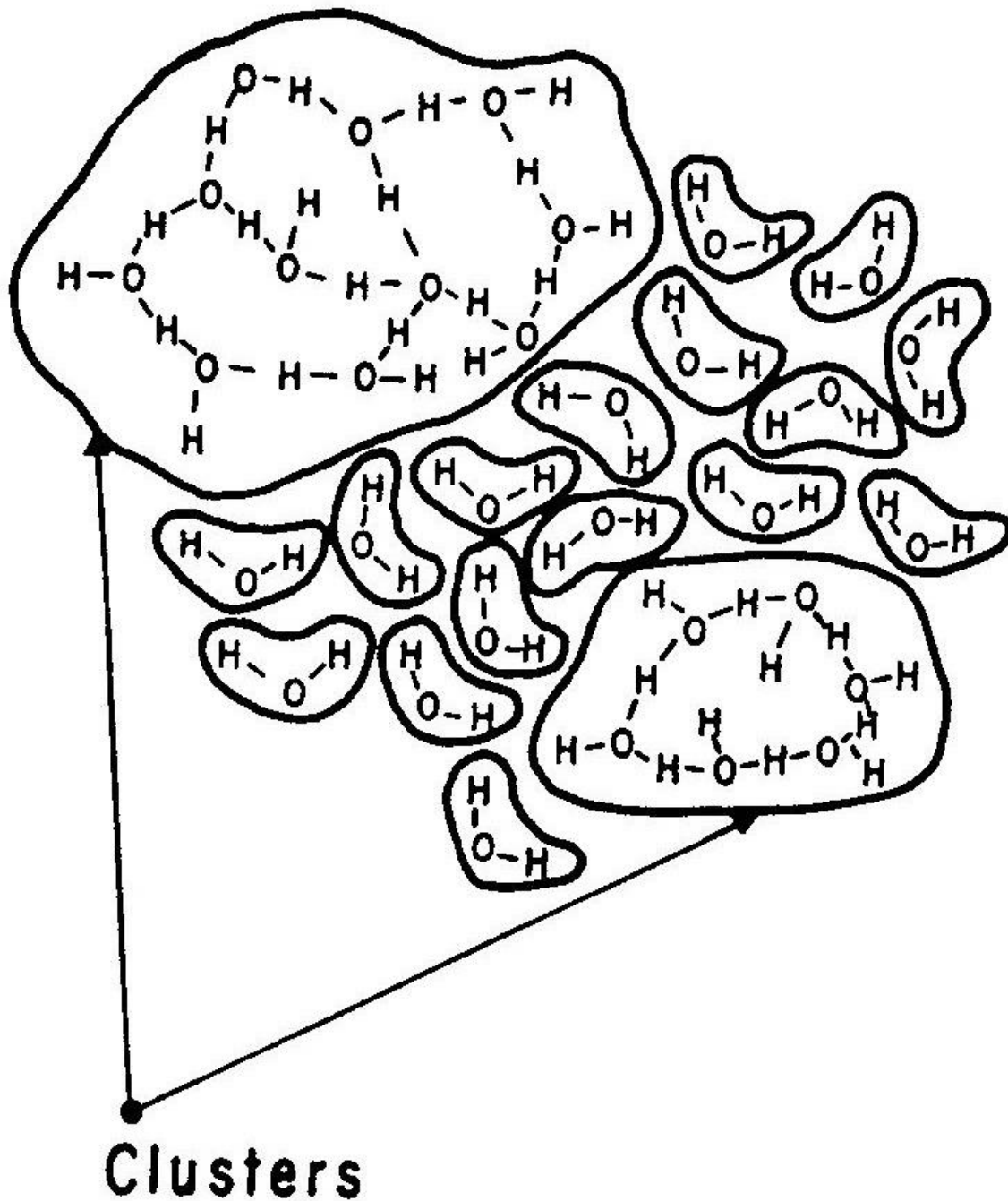


Hydrogen bonding
in liquid water is
always present

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

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(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

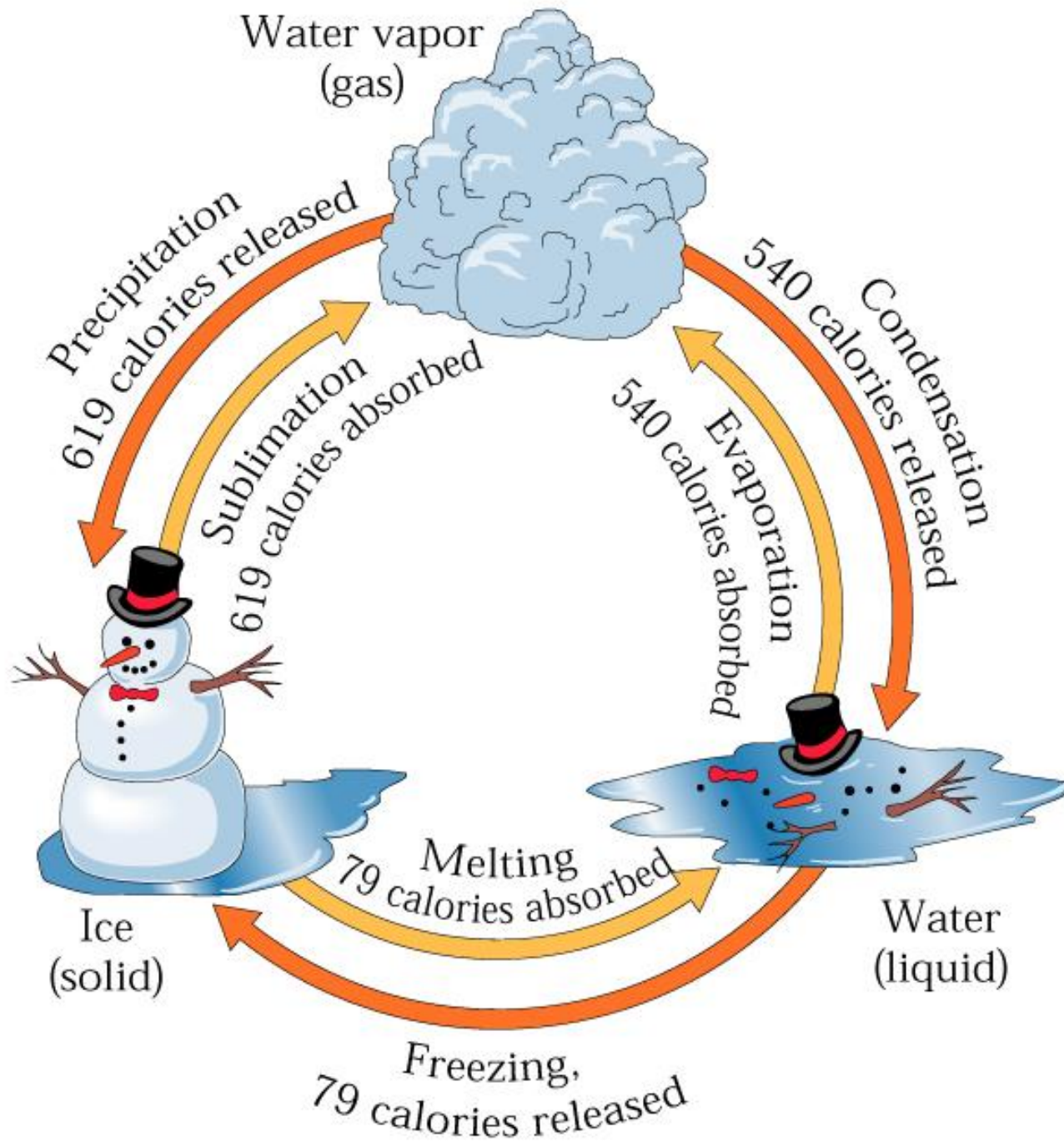
High Heat of Vaporization
($\Delta H = 540 \text{ cal/g}$)

(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

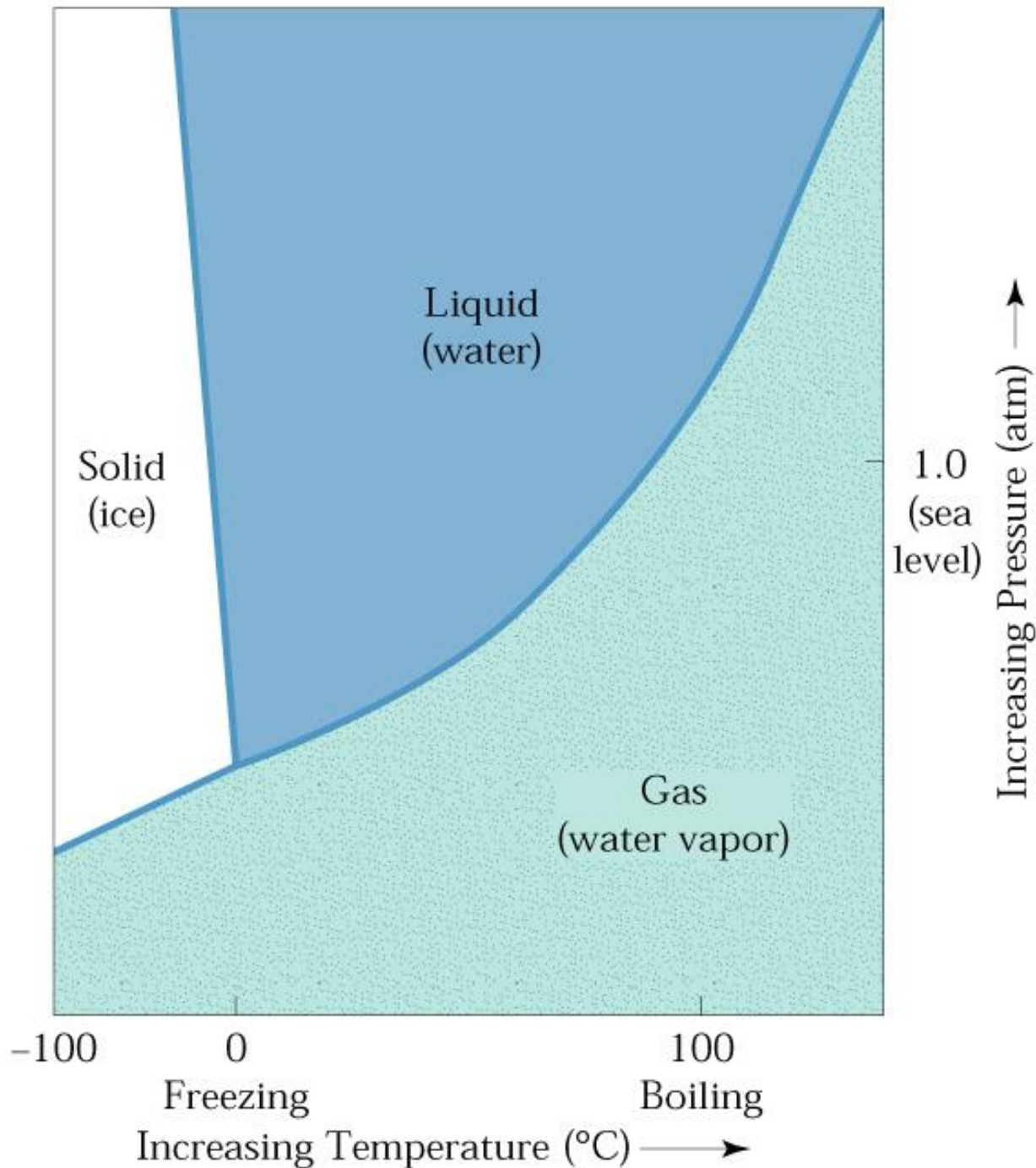
Water Properties

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

