Chemical Oceanography

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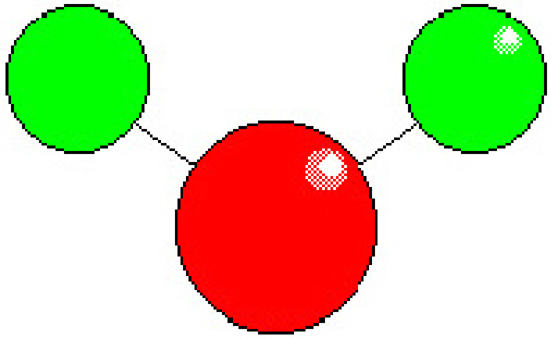
Water –
Amazing Stuff

Chemical Oceanography

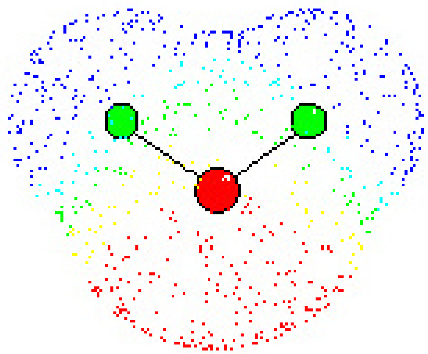
Physical Chemistry of Seawater (Millero Chap. 4)

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

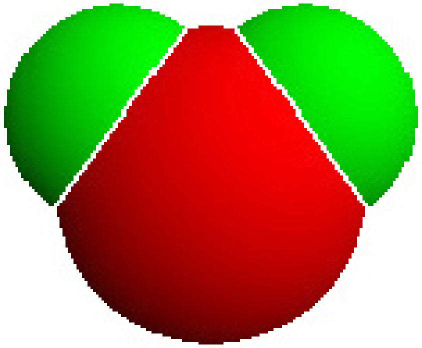
Molecular Structure of H_2O



"Ball & Stick" Model



Electron Density Distribution



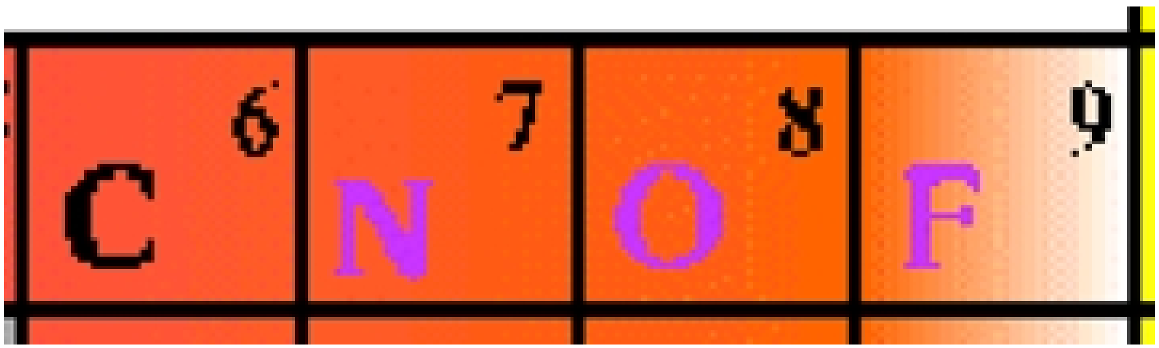
Space Filling Model

Periodic Table of the Elements

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

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

Zoom in on O
and its neighbors



Each can form compounds with hydrogen

Boiling Point Comparison from Millero

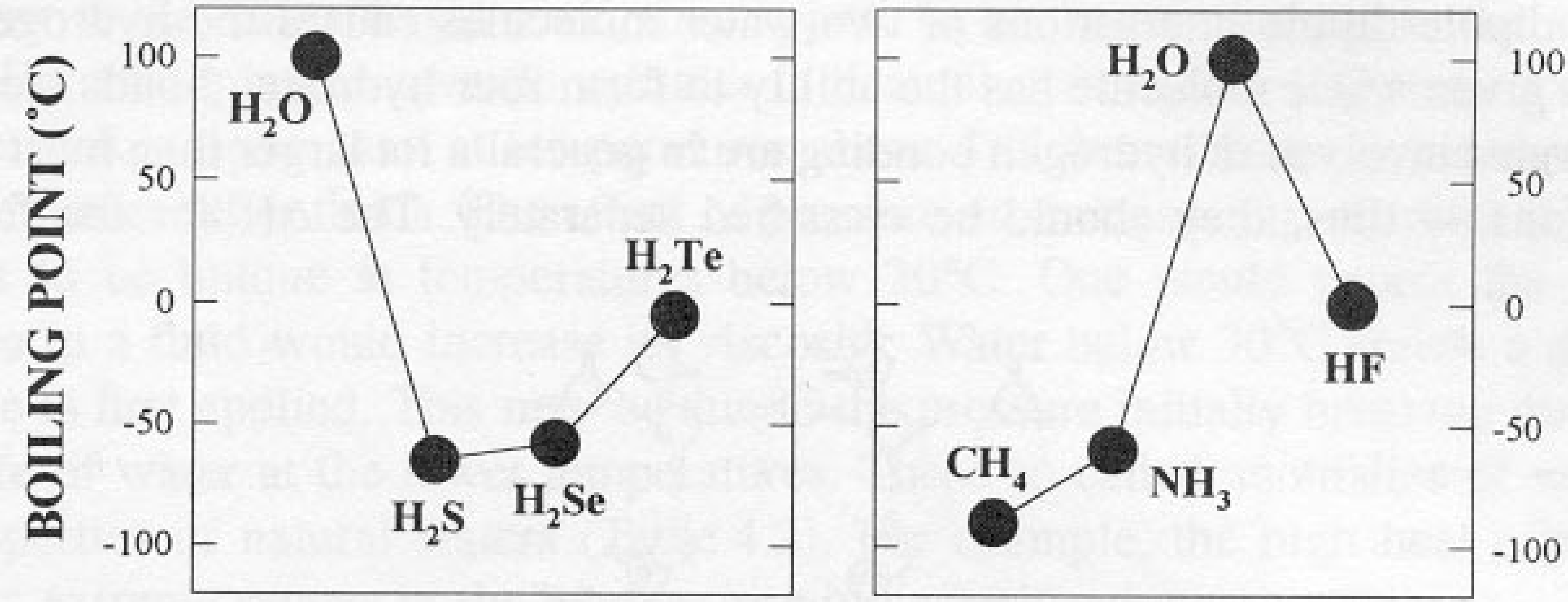
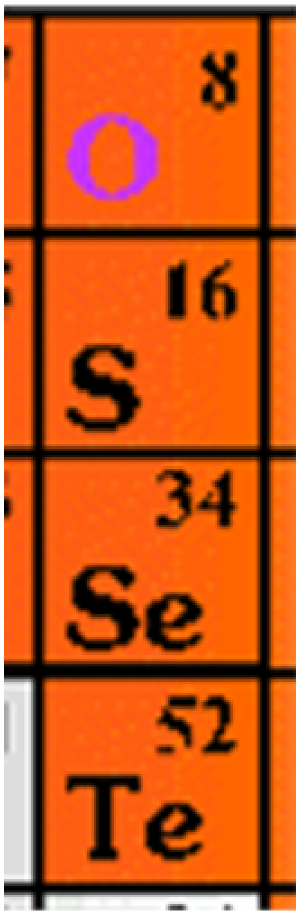


FIGURE 4.1. Boiling points of compounds structurally similar to water.

Look at O and its relatives



Outer shell electronic Configuration is the same

Boiling Point Comparison from Millero

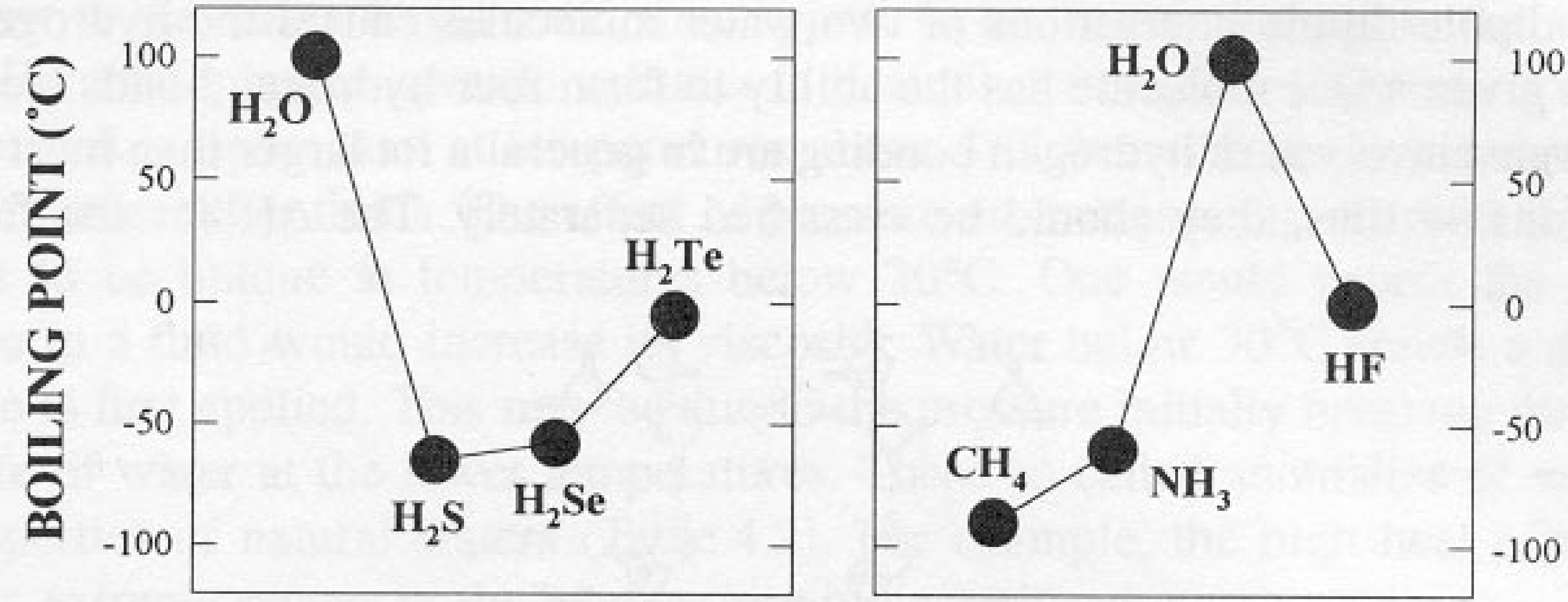
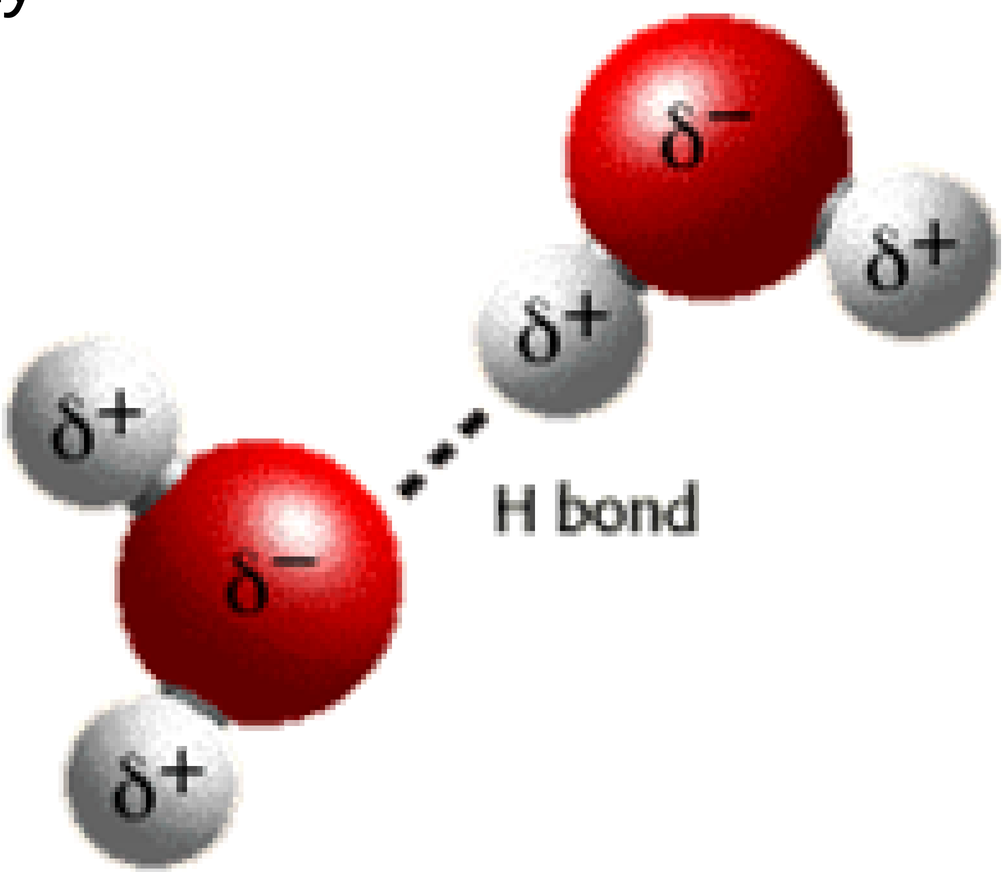


FIGURE 4.1. Boiling points of compounds structurally similar to water.

Hydrogen Bonding is key to anomolous properties of water

H-Bonding results from polarity



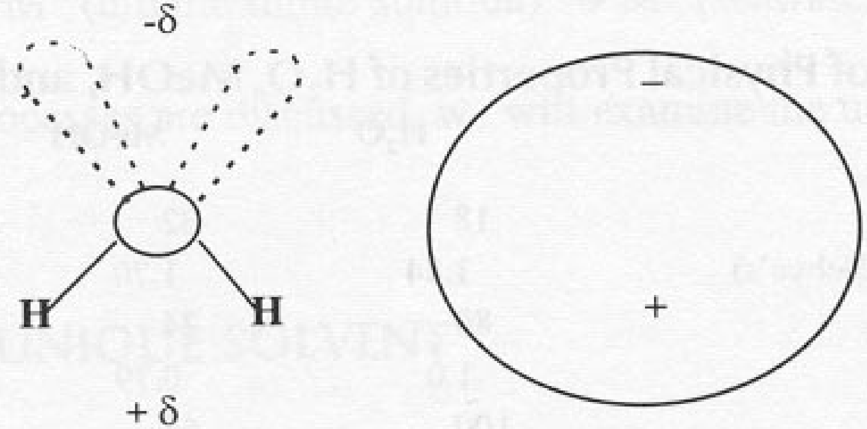


FIGURE 4.3. The water dipole.

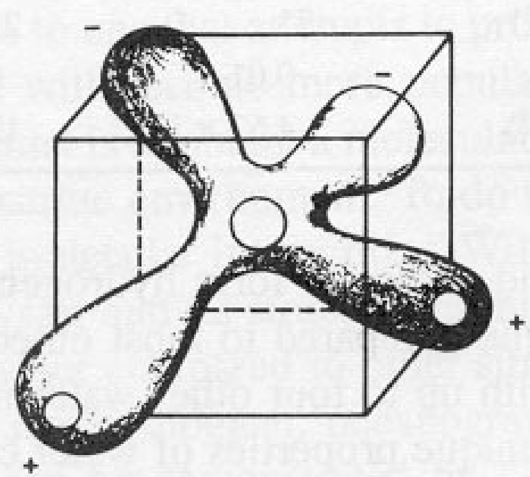
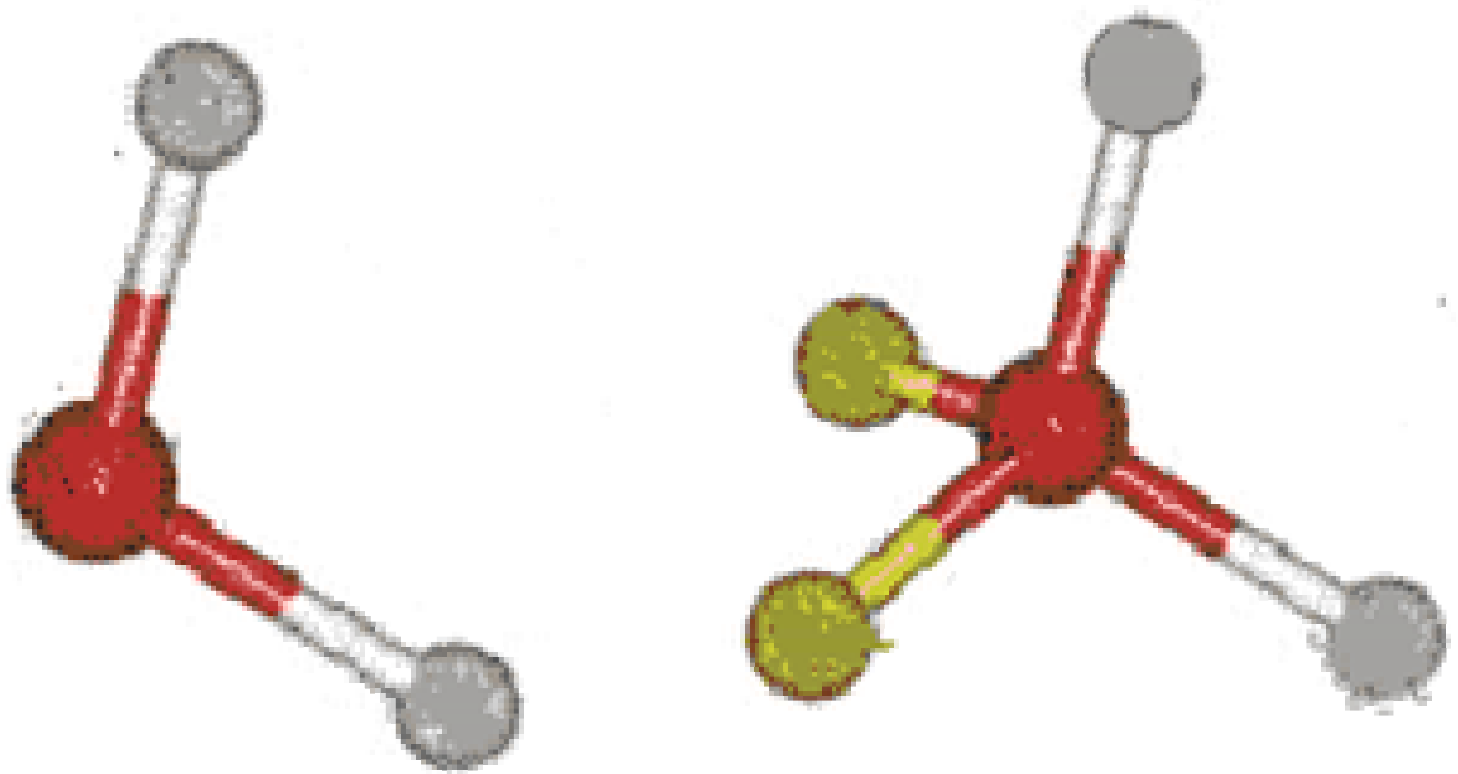


FIGURE 4.4. The three-dimensional structure of the water molecule.

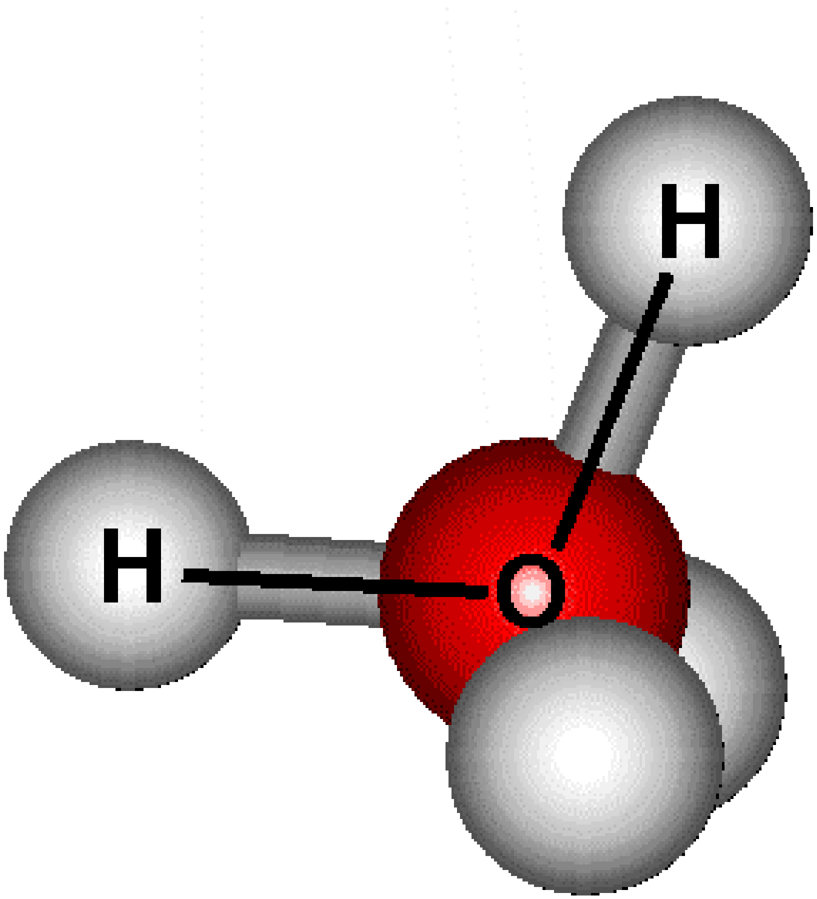
Dipole & Quadrapole Diagrams (Millero)

Water dipole & quadrapole

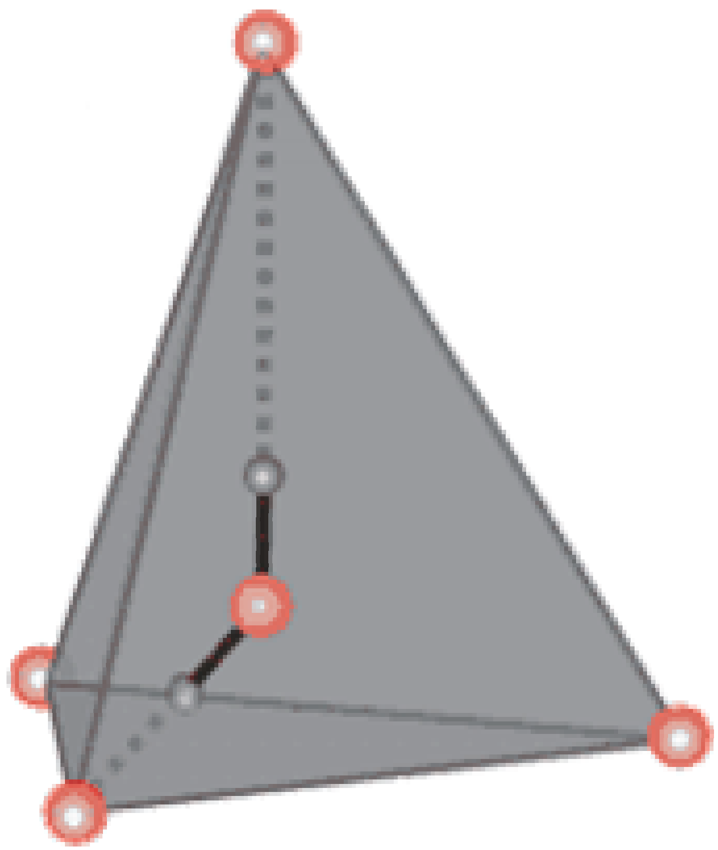


Oxygen is shown in red, Hydrogen is shown in gray & Electrons are depicted as yellow

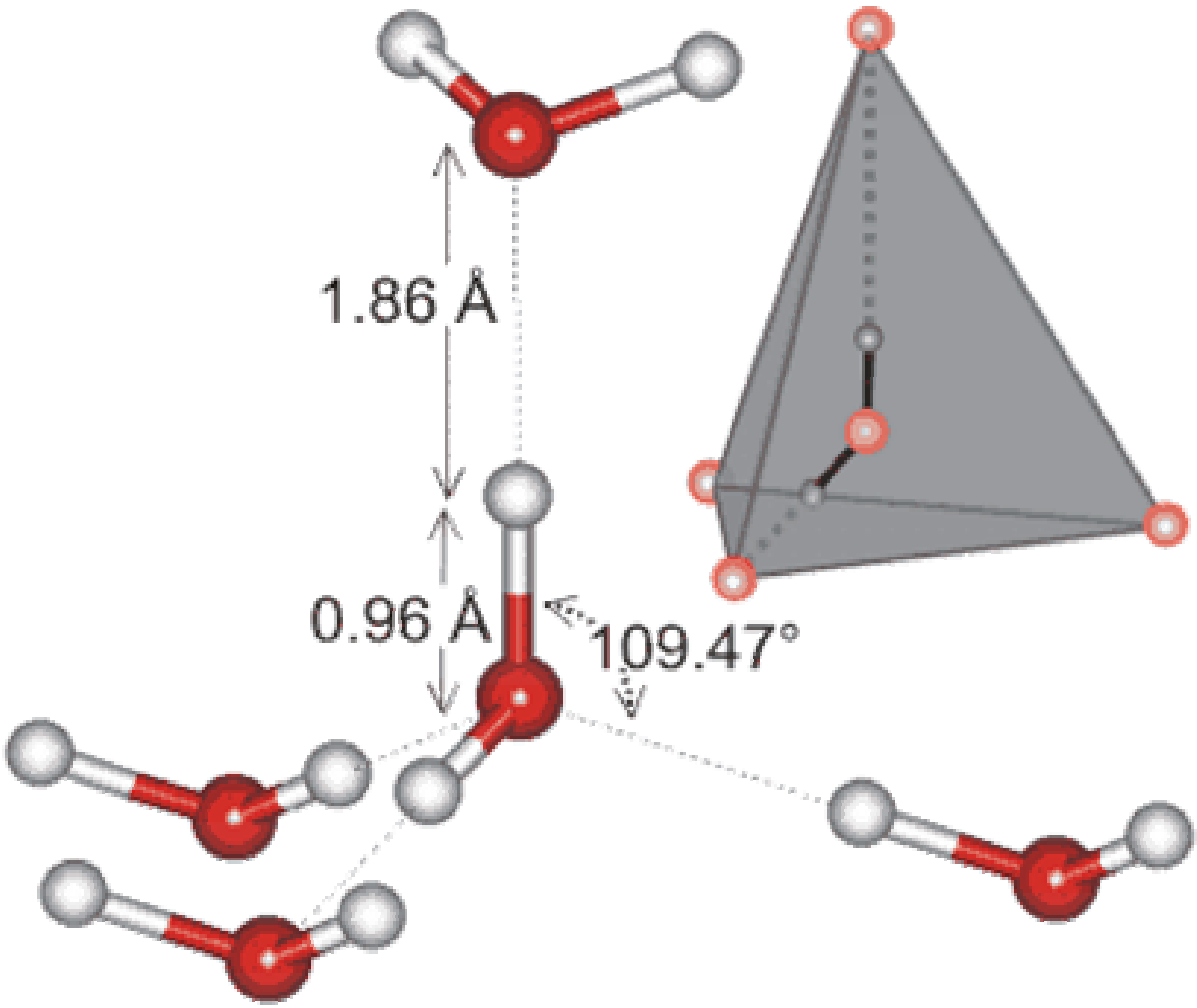
Yet another representation



Water Tetrahedron



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



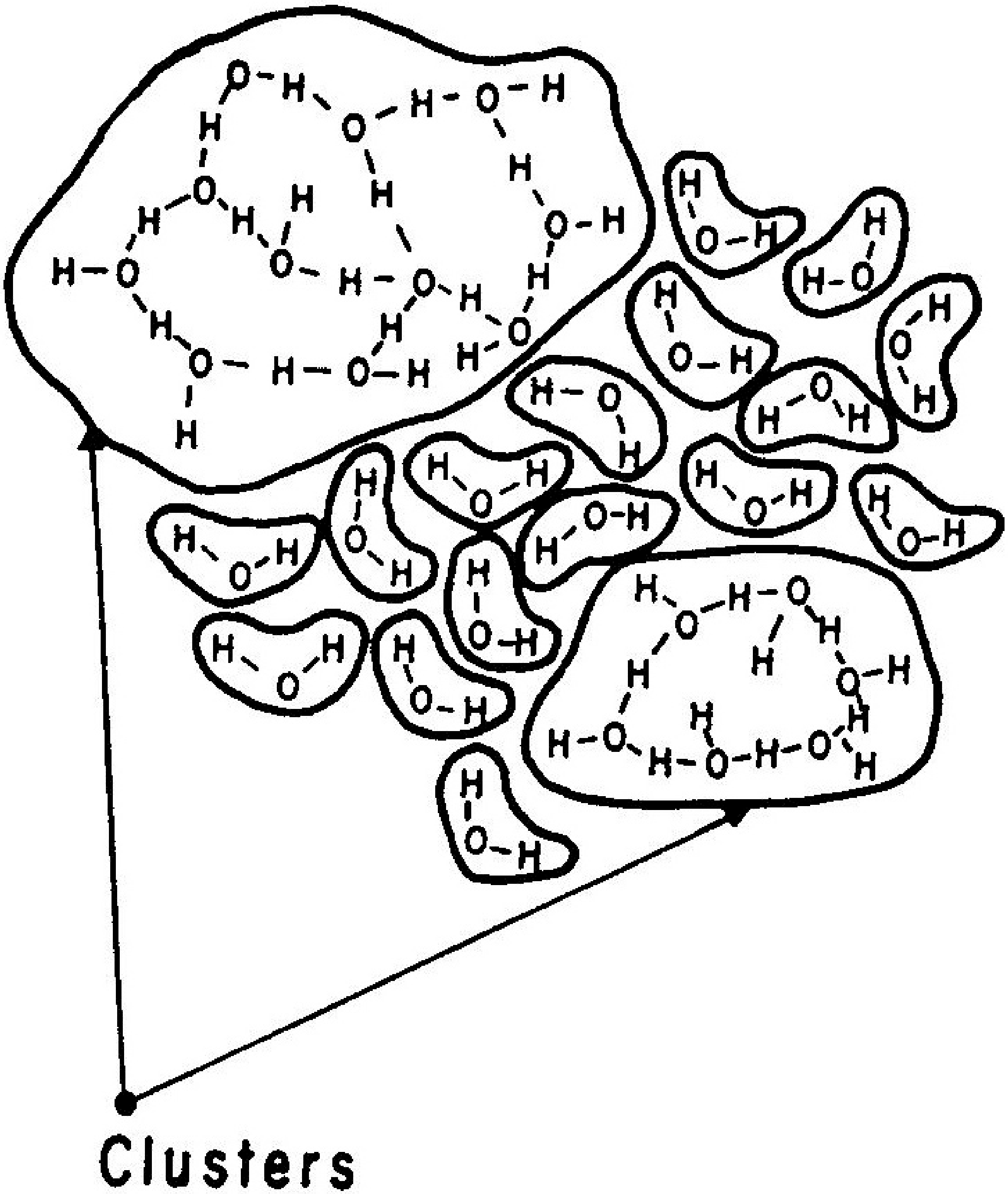
Arrangement for Hydrogen Bonding - Pentamer

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 p 130–134 for models



Water Clusters Dynamically Form, Break and Re-form

Frank & Wen
Flickering Cluster Model

(Millero 1996)

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

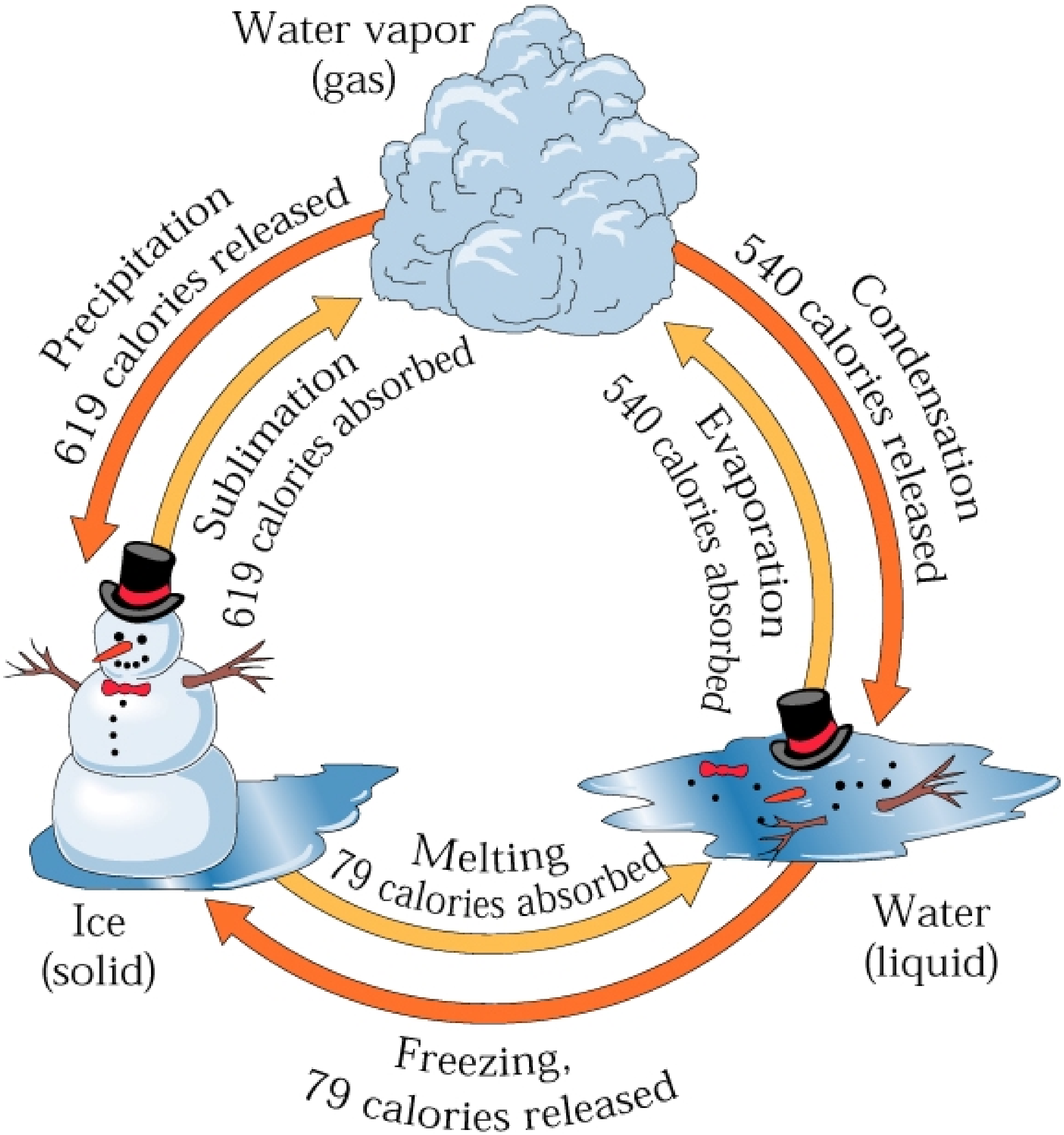
Water Properties

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

(Heat energy for evaporating liquid)

Highest of all liquids

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



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

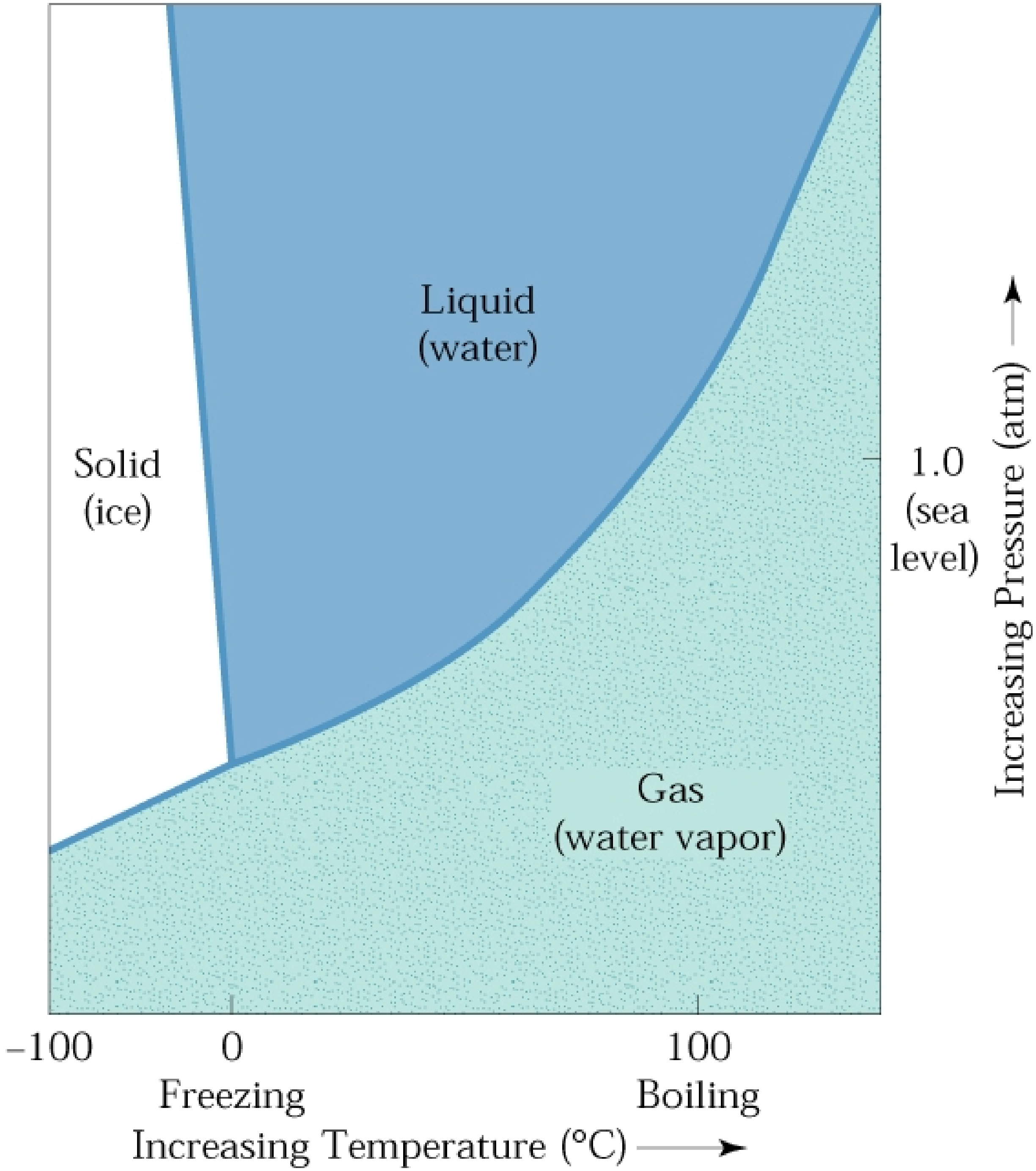
Ice floats

Water Properties

Boiling & Freezing Points

(much higher than expected or projected)

Water exists in 3 phases in critical temperature range for life



Simple Phase Diagram of Water

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

Water Properties

High Heat Conduction

(highest of all liquids)

Important for small scale heat transfer as in cells

Water Properties

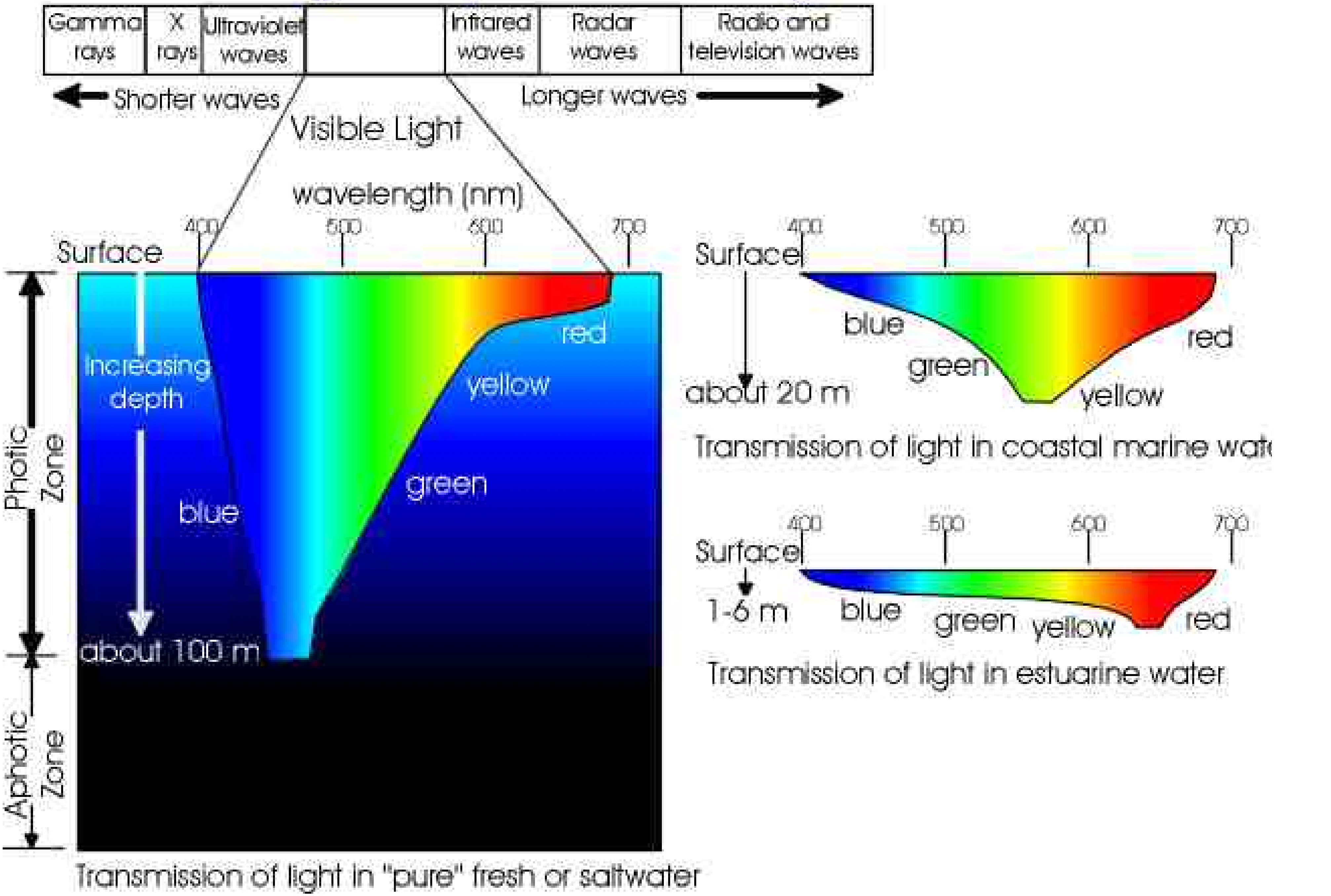
High Transparency

(absorption of radiant energy high in IR and UV)

Water is colorless

Important in photosynthetic and photochemical processes

Electromagnetic spectrum of sunlight



Water Properties

Low Electrolytic Dissociation

(neutral molecule containing some OH^- and H^+)

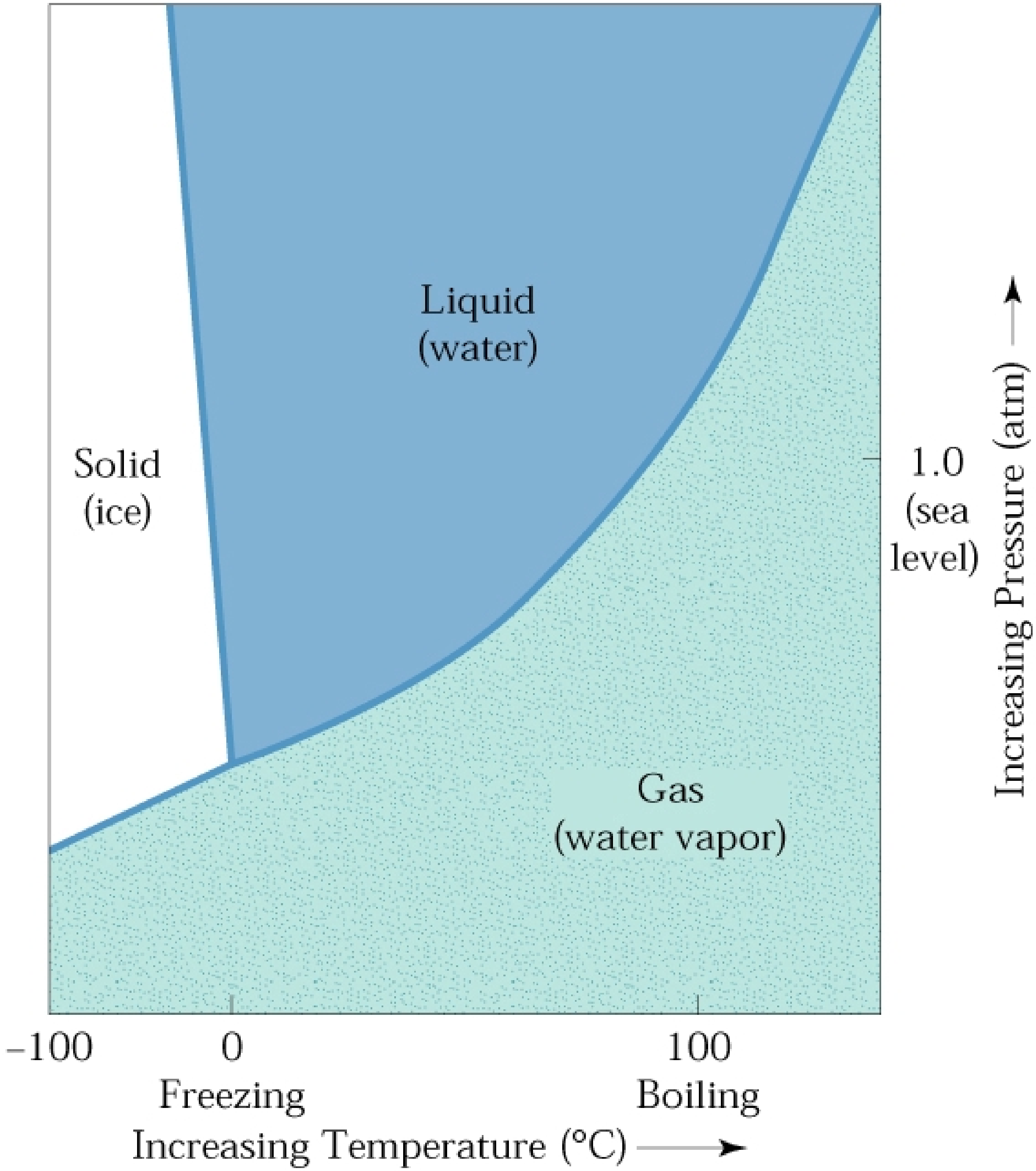
Autodissociation of water important in acid-base chemistry, many geological and biological processes

Water Properties

Low Compressibility

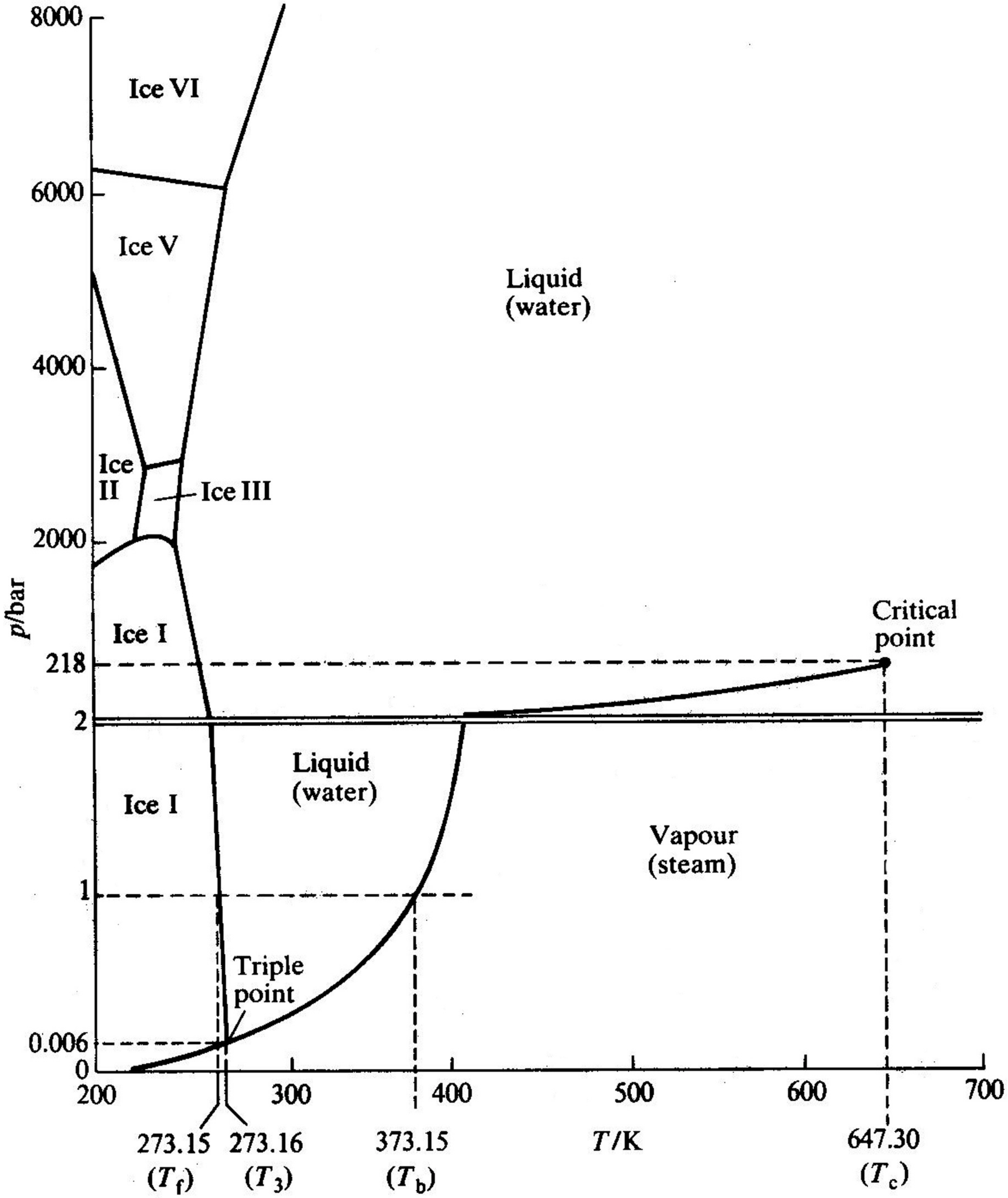
(similar to solids)

Little change in density as pressure increases with depth



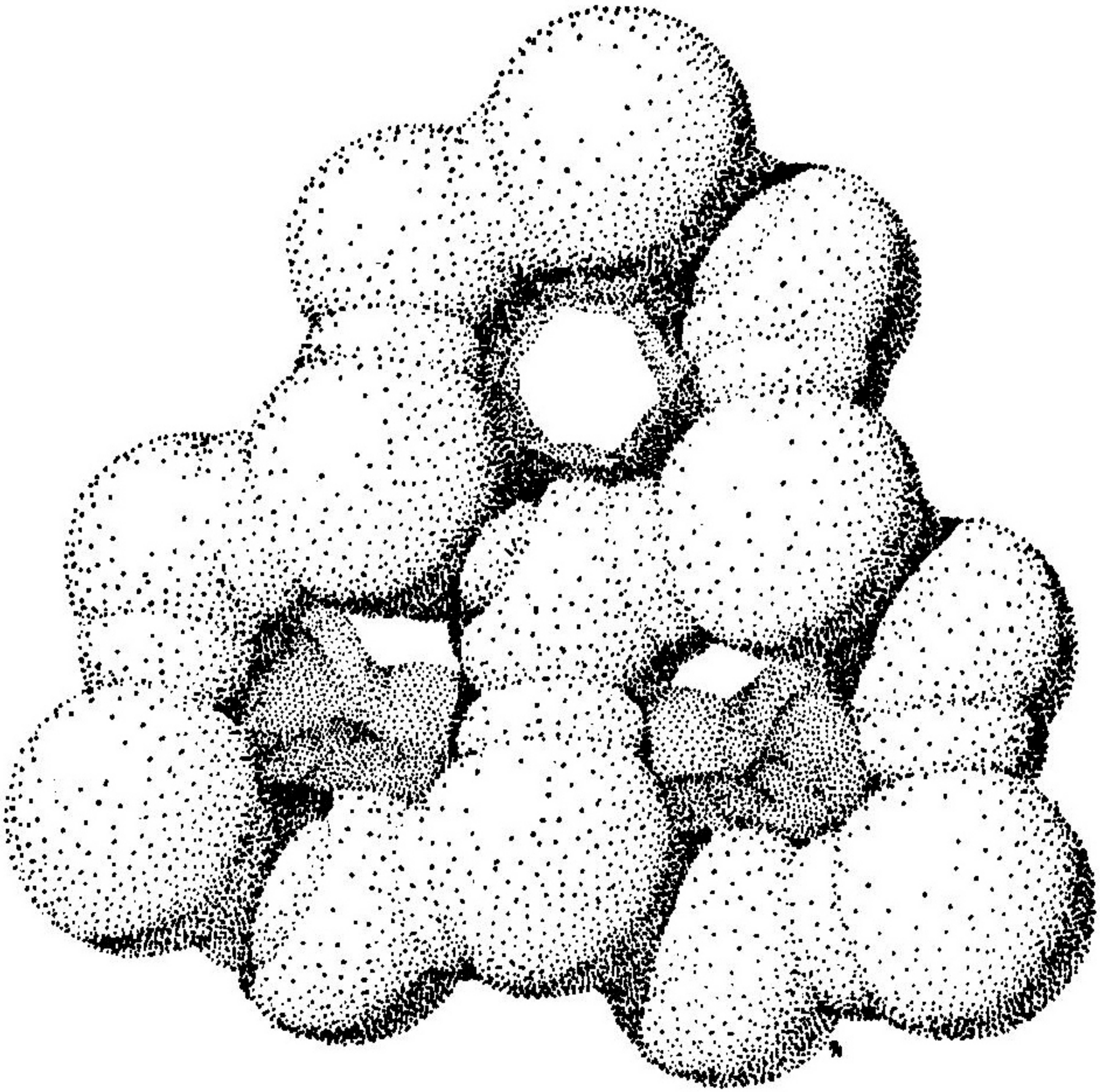
Simple Phase Diagram of Water

(Wiley 1999)



Detailed Phase Diagram of Water Showing Forms of Ice

(Atkins 1990)

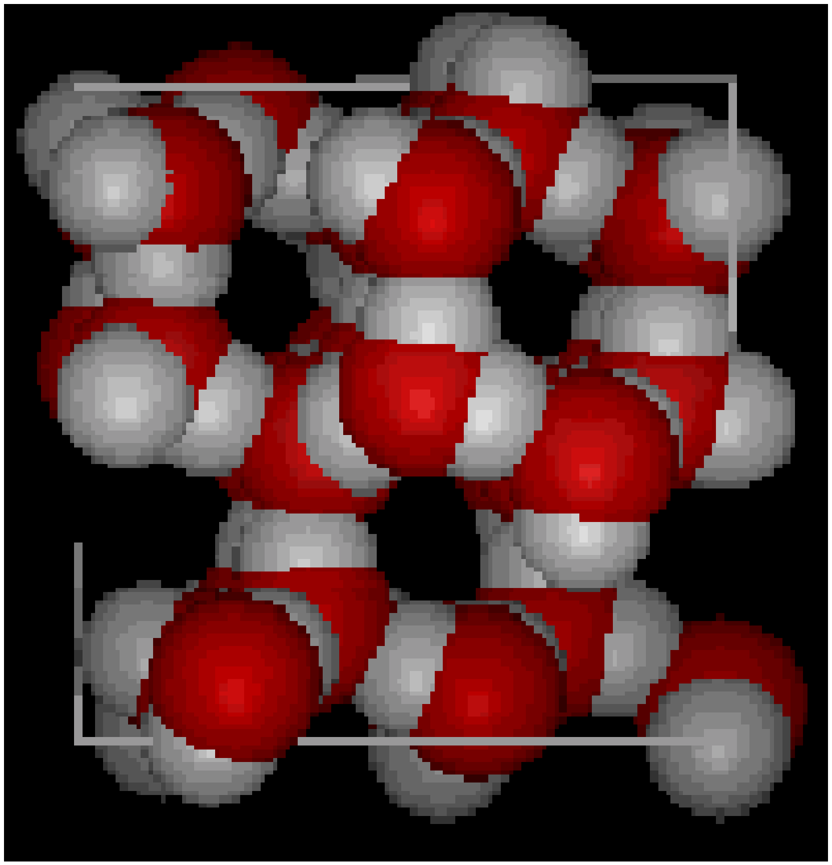


Structure of Ice 1h, Hexagonal with Space Giving Low Density

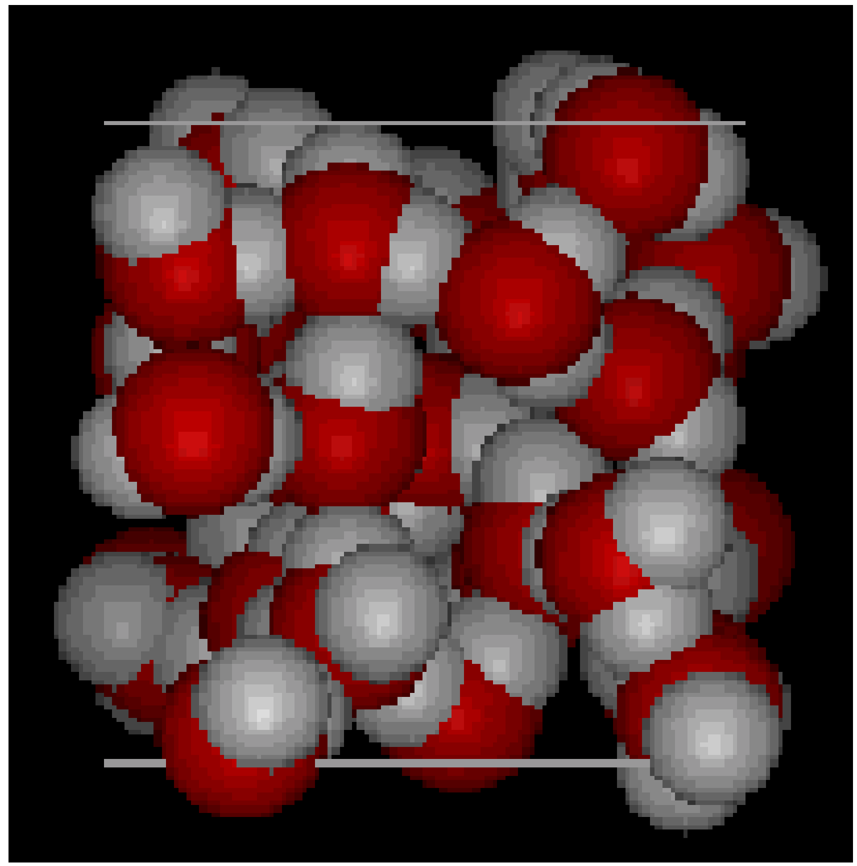
(Pilson 1998)

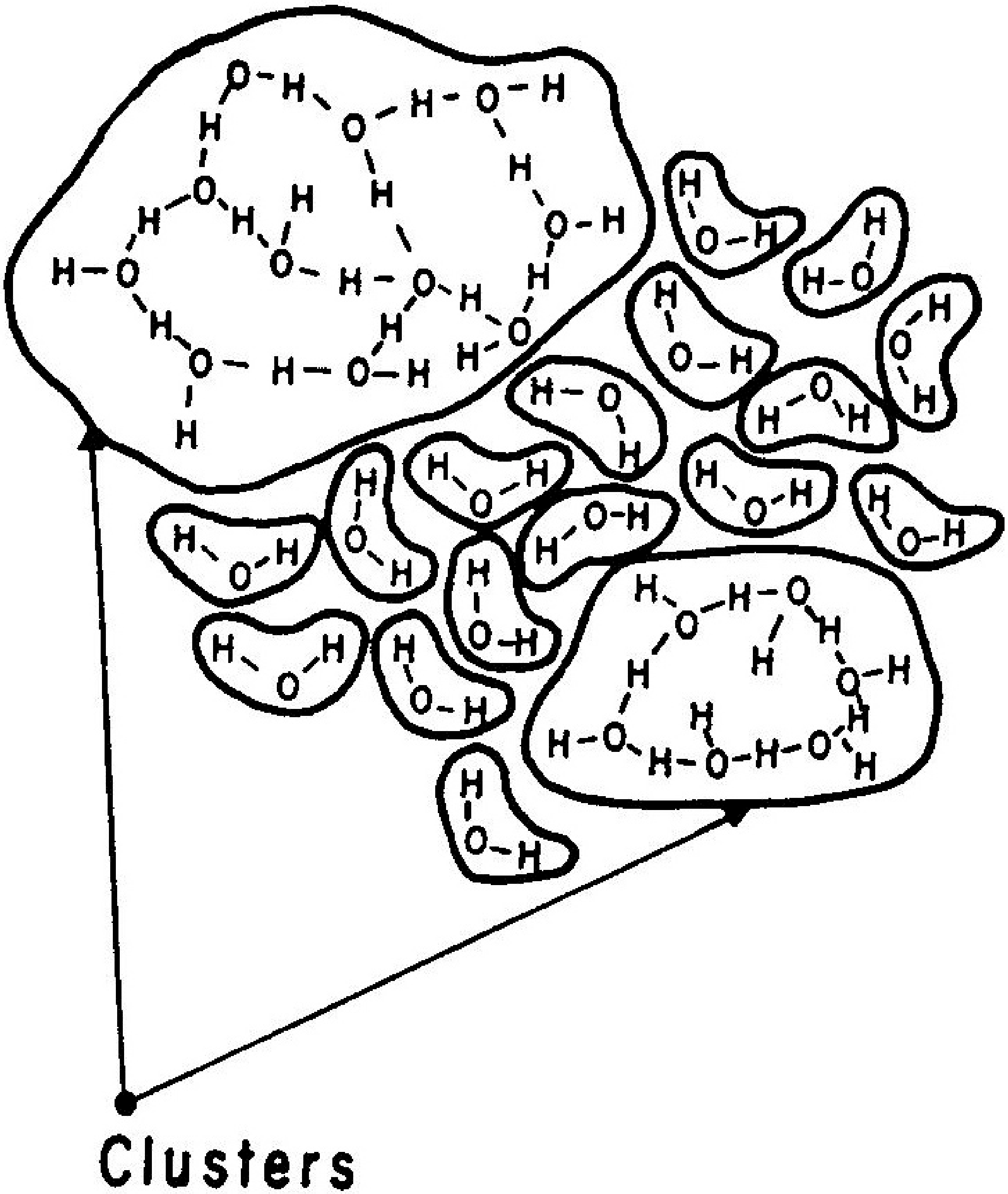
Comparison of Ice and Liquid Water Structures (NYU-SVL)

Ice 1h



Liquid Water

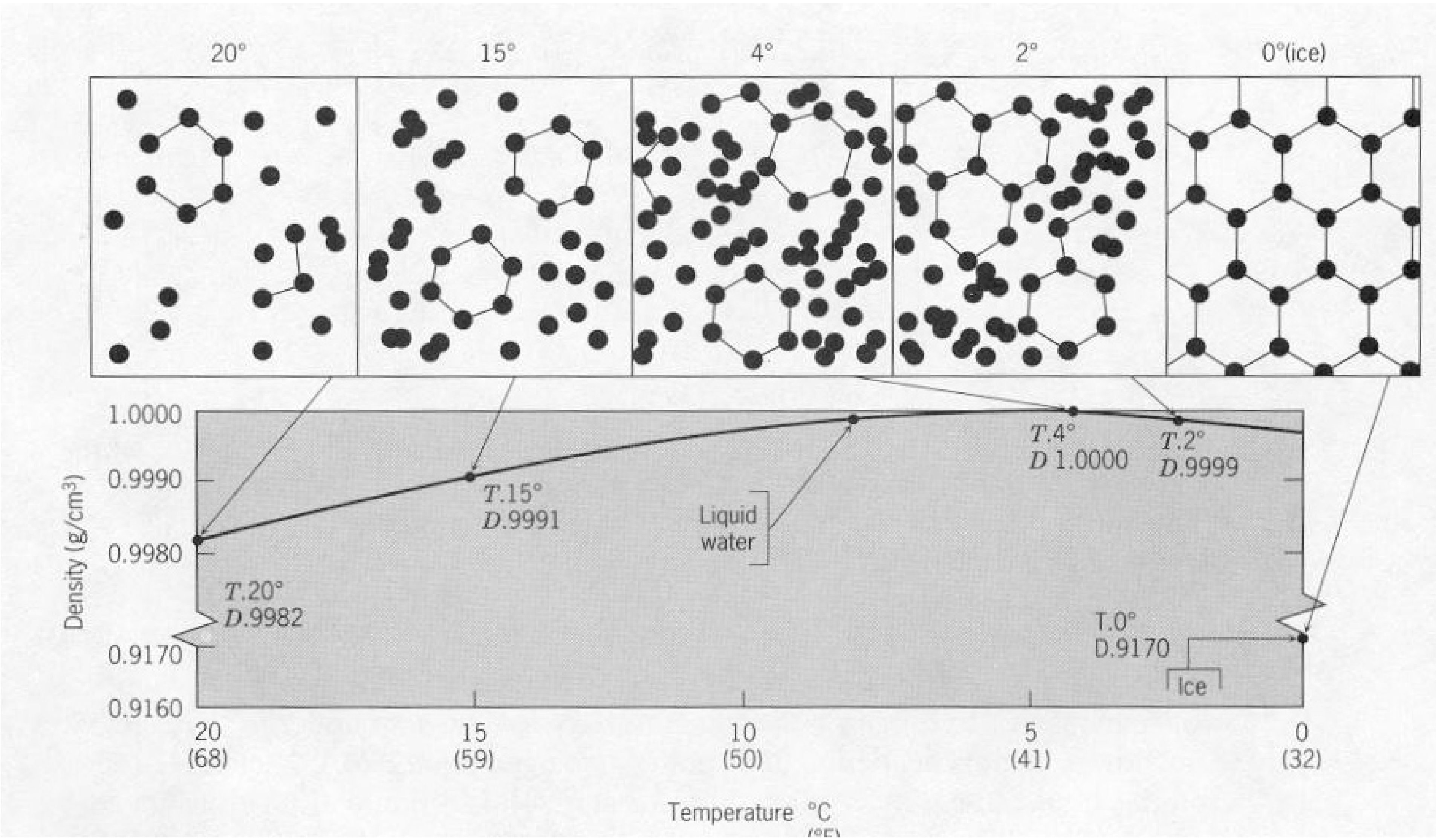




Water Clusters Dynamically Form, Break and Re-form

(Millero 1996)

Structure or Association of Water Molecules Versus Temperature and Affect on Density (Libes 1992)



What happens when we add solutes to water?

**“Water, water, every where,
Nor any drop to drink.”**

The Rime of the Ancient Mariner

Samuel Taylor Coleridge

Circa 1798

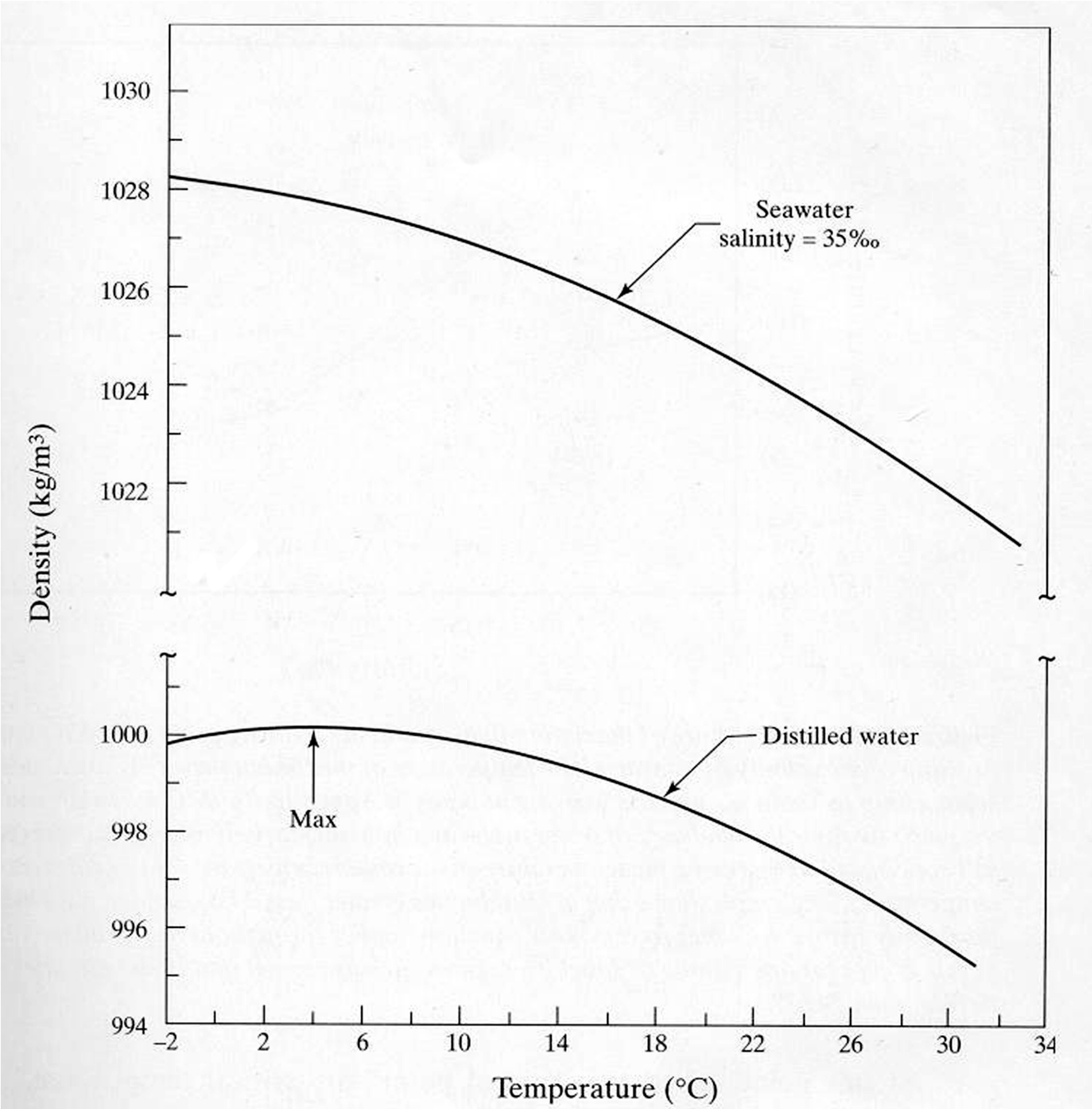
Solutes (Particularly Ions) are Structure Breakers

- More accurately they form new structures
- Reorient some water molecules
- Cause new associations
- Modify properties
- Alter much of the Physical Chem. (Physicochemical Properties)

Websites of interest Re: H_2O

- 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
- www.sbu.ac.uk/water

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



Temperature Density Diagram for Pure Water & Seawater at 35 PSU

(Pilson 1998)

TABLE 2.2
Comparison of Pure Water and Seawater Properties

Property	*Seawater, 35‰ S*	*Pure Water*
Density, g/cm^3, 25°C	1.02412	1.0029
Equivalent conductivity, 25°C, $cm^2\ ohm^{-1}\ equiv^{-1}$	—	—
Specific conductivity, 25°C, $ohm^{-1}\ cm^{-1}$	0.0532	—
Viscosity, 25°C, millipoise	9.02	8.90
Vapor pressure, mm Hg at 20°C	17.4	17.34
Isothermal compressibility, 0°C, unit vol/atm	46.4×10^{-6}	50.3×10^{-6}
Temperature of maximum density, °C	−3.52	+3.98
Freezing point, °C	−1.91	0.00
Surface tension, 25°C, dyne/cm	72.74	71.97
Velocity of sound, 0°C, m/s	1450	1407
Specific heat, 17.5°C, $J\ g^{-1}{}^{\circ}C^{-1}$	3.898	4.182

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Some Properties Undergo Dramatic Changes

Website for Millero 1996 & Periodic Tables

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

www.mbari.org/chemsensor/pteo.htm

http://earth.agu.org/eos_elec/97025e.html