Chemical Oceanography

Dr. David K. Ryan
Department of Chemistry
University of Massachusetts Lowell
&
Intercampus of Marine Sciences Program

http://faculty.uml.edu/David_Ryan/84.653

Water –
Amazing Stuff

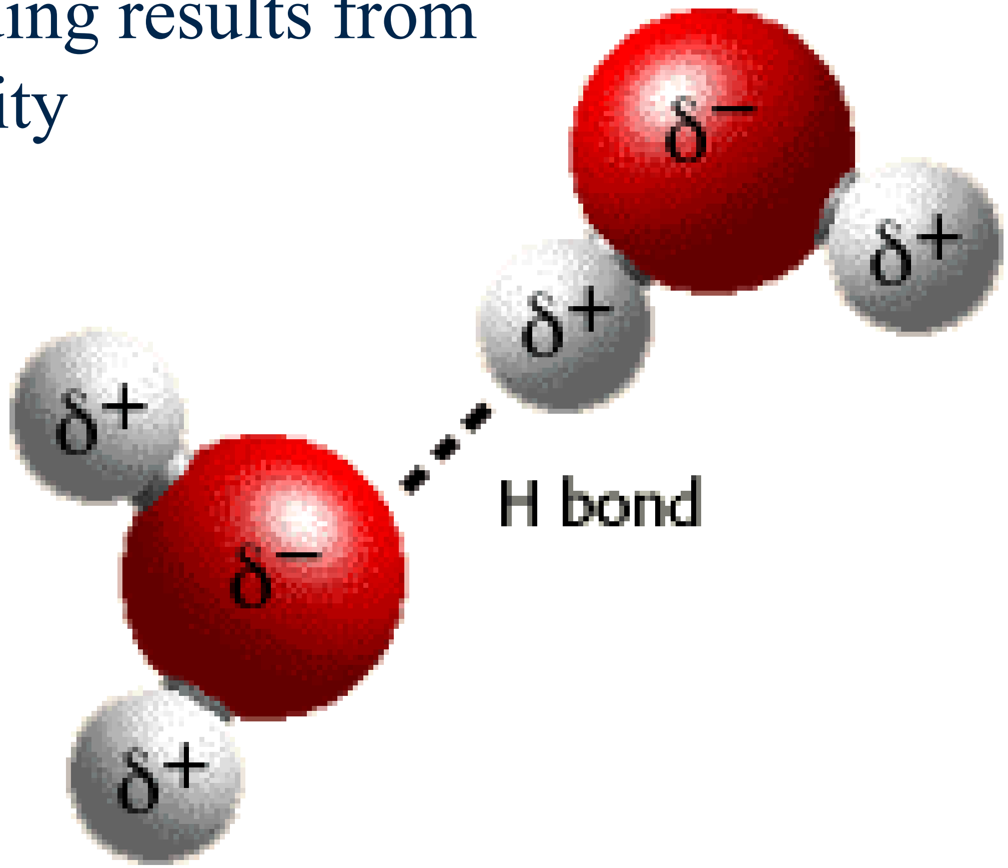
Chemical Oceanography

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

Hydrogen Bonding is key to anomalous properties of water

H-Bonding results from polarity



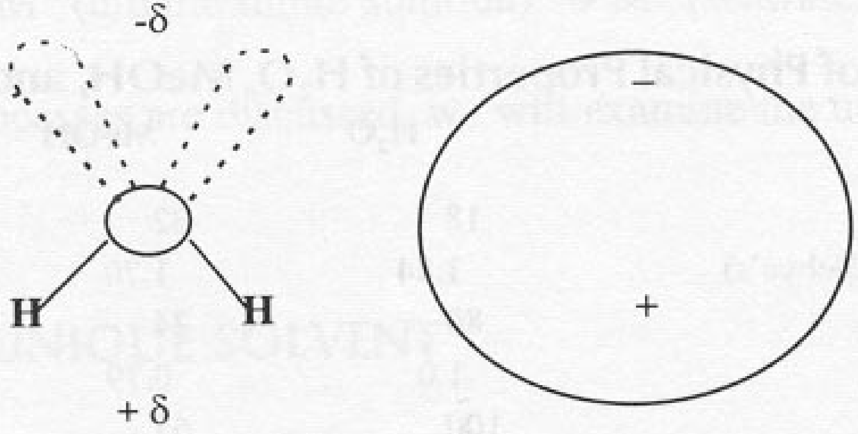


FIGURE 4.3. The water dipole.

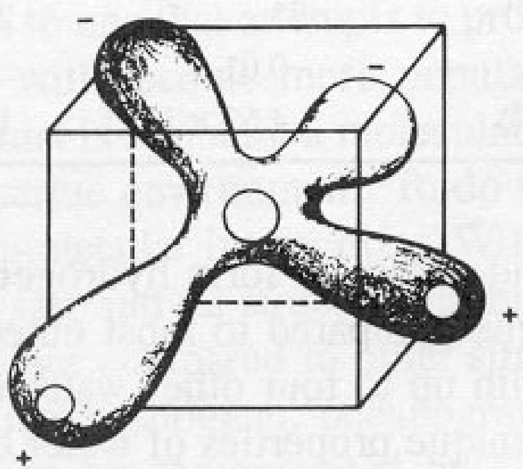
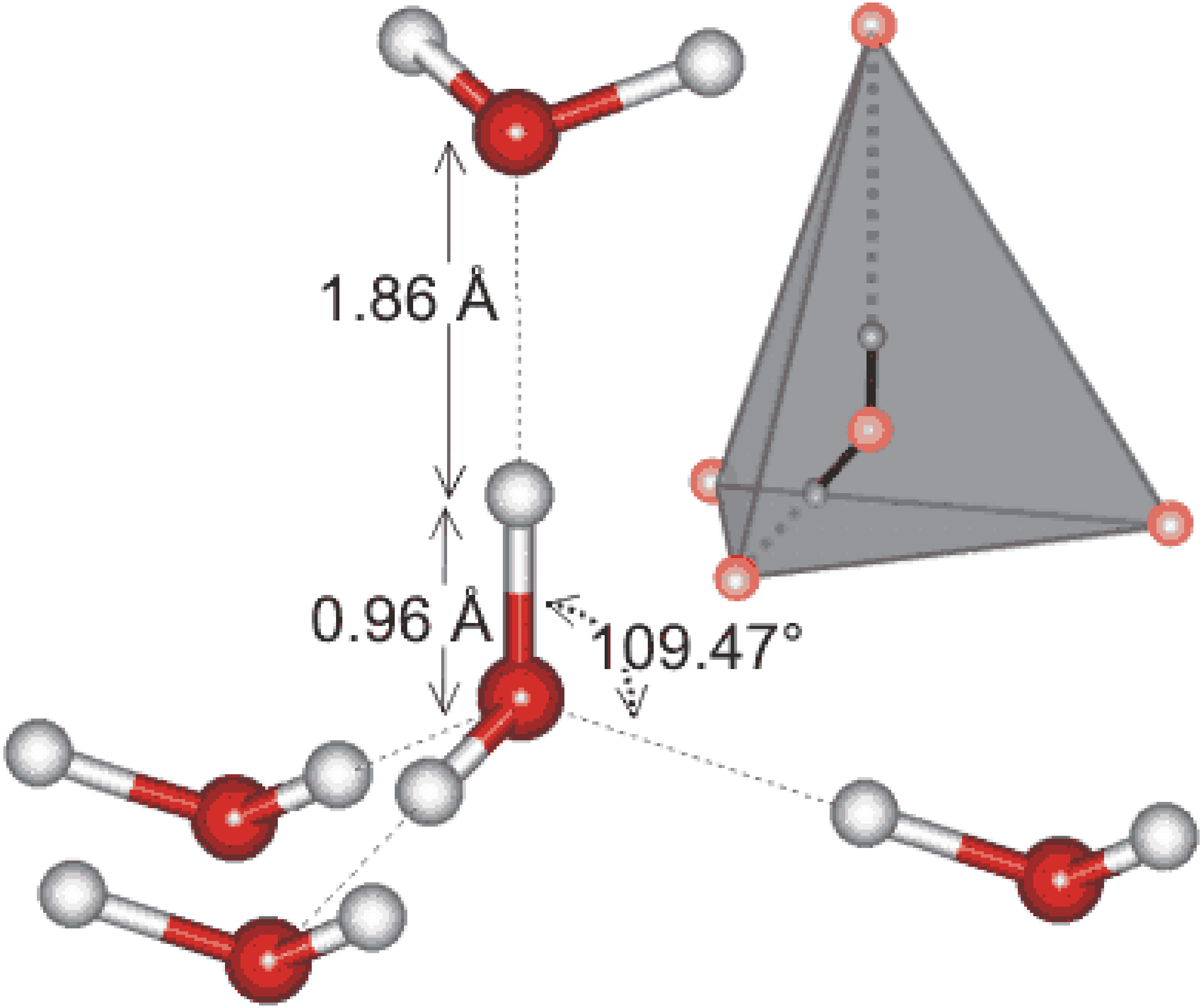


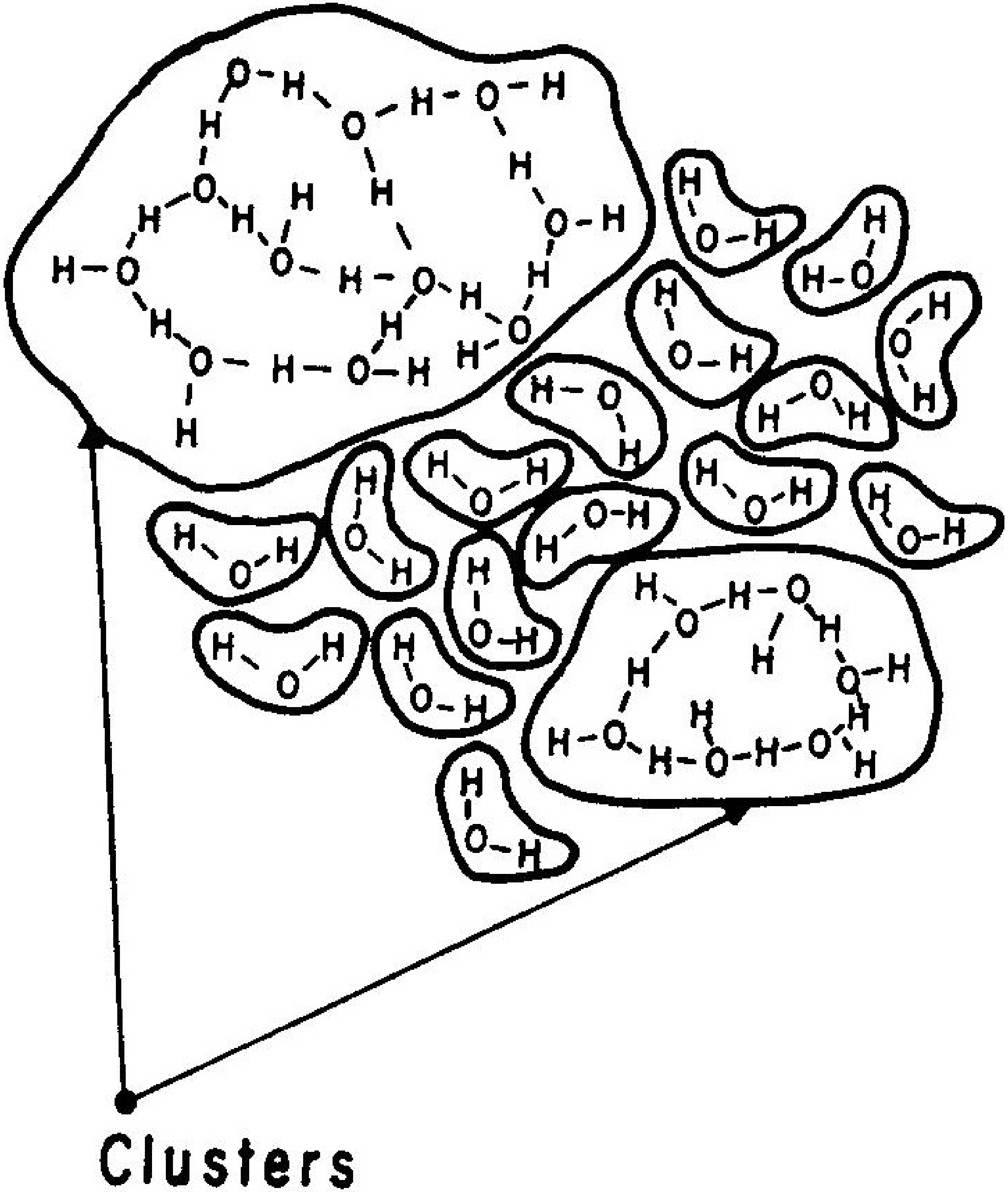
FIGURE 4.4. The three-dimensional structure of the water molecule.

Dipole & Quadrapole Diagrams

(Millero 2006) p. 125



Arrangement for Hydrogen Bonding - Pentamer



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

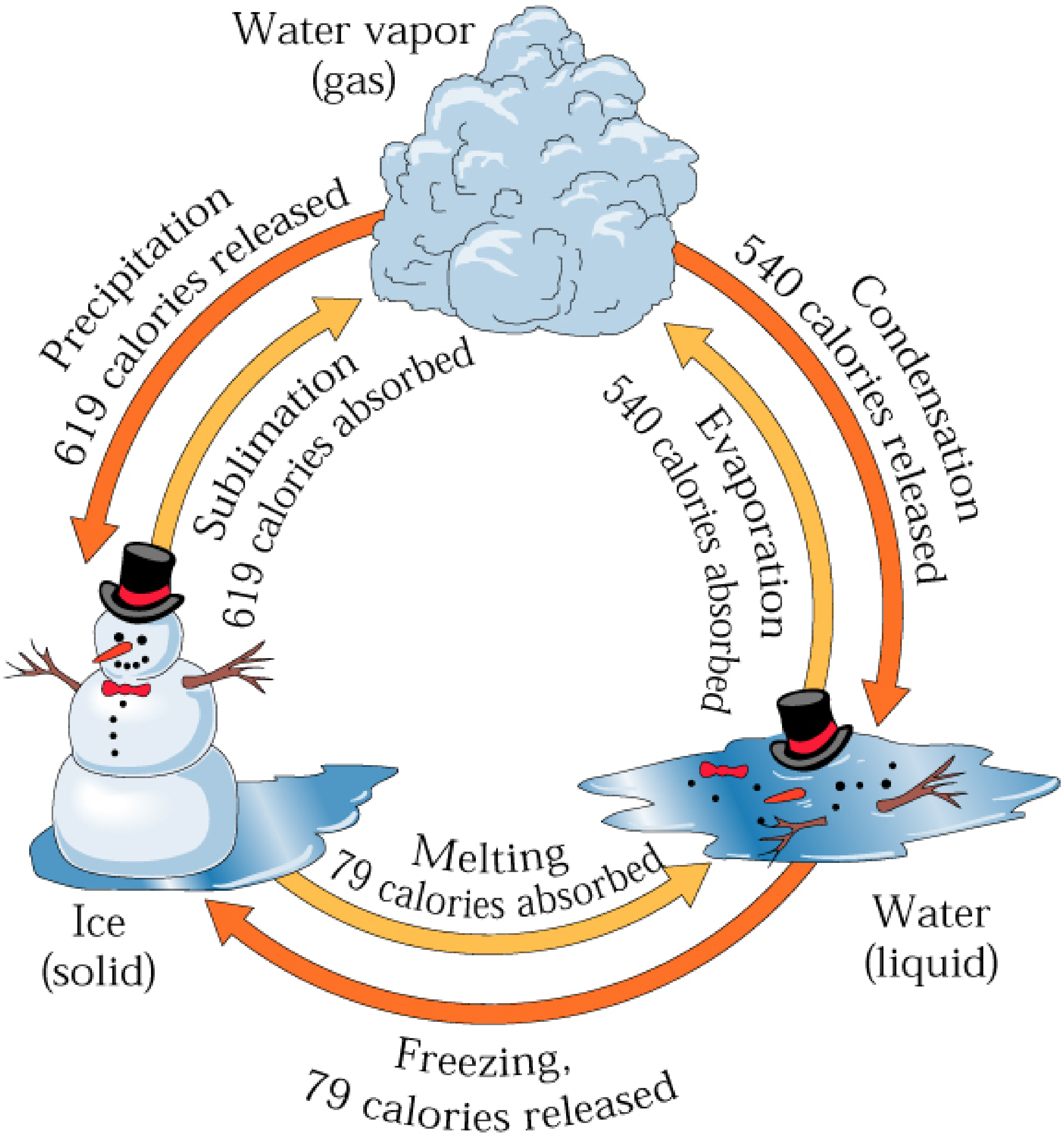
($\Delta H = 540$ cal/g)

(Heat energy for evaporating liquid)

Highest of all liquids

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

a.k.a. Enthalpy of Vaporization



Large Quantities of Heat are Absorbed & Released During Phase Changes

(Wiley 1999)

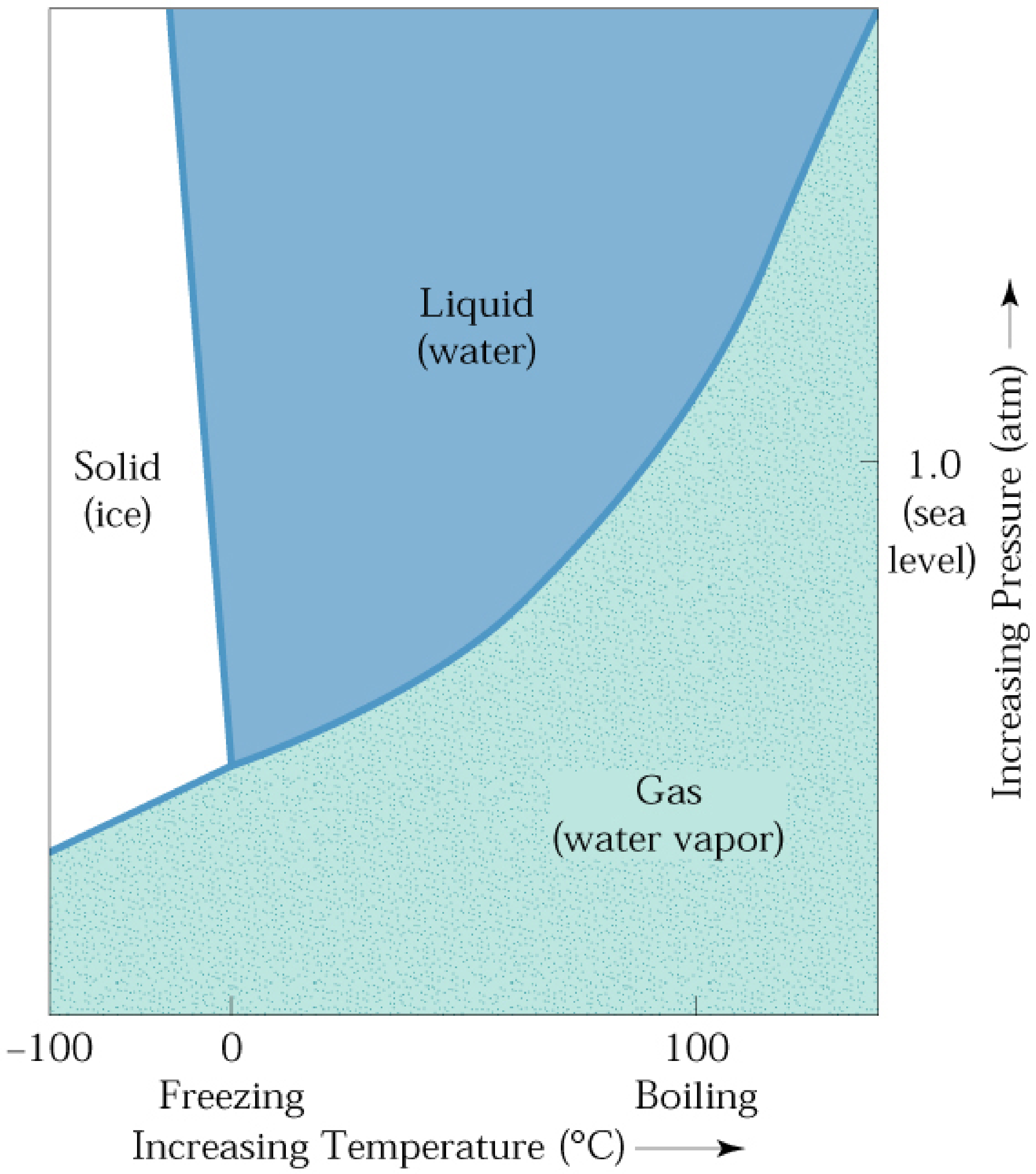
Water Properties

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

Water Properties

High Heat Conduction

(highest of all liquids)

Important for small scale heat transfer as in cells

Water Properties

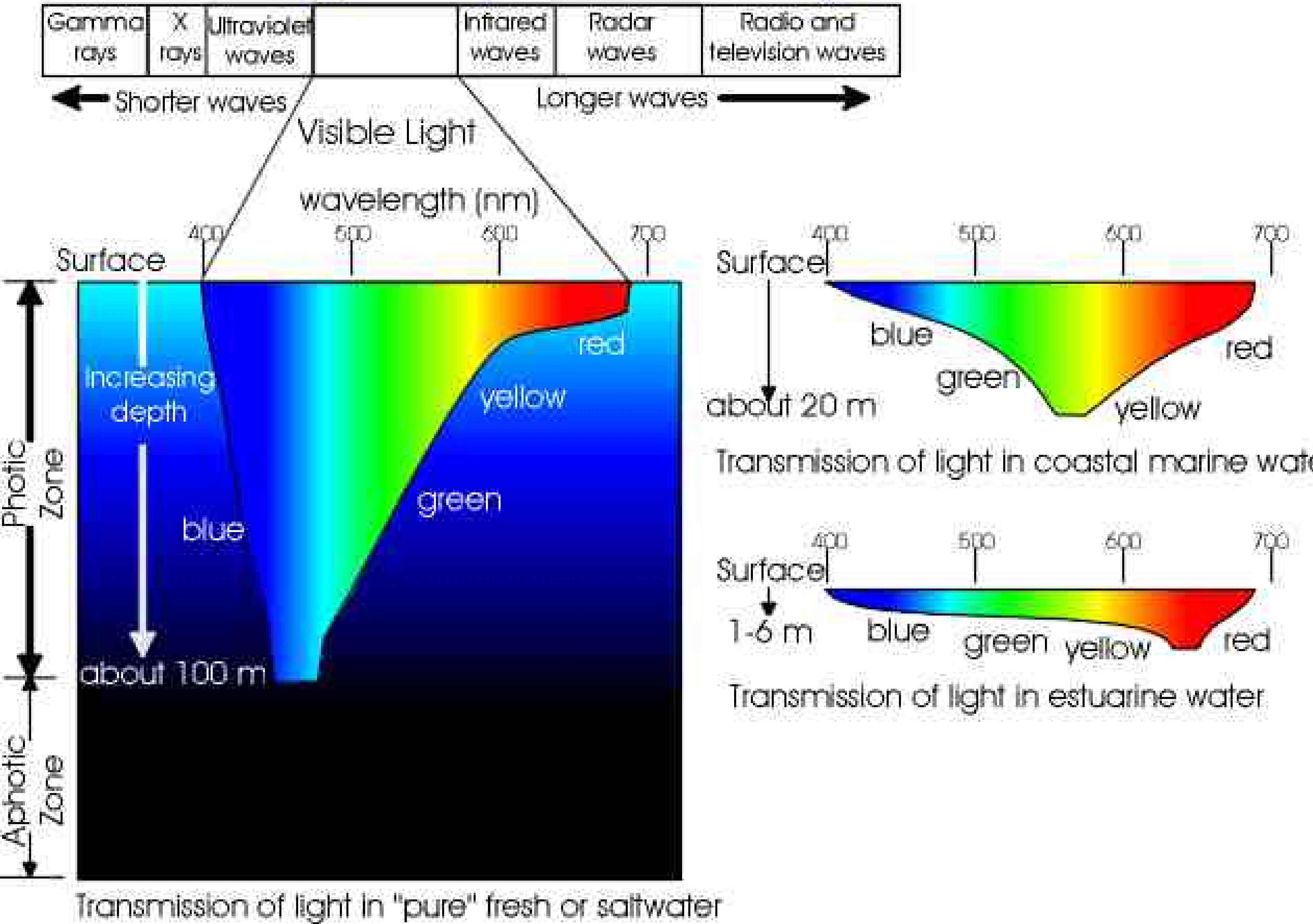
High Transparency

(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^+)

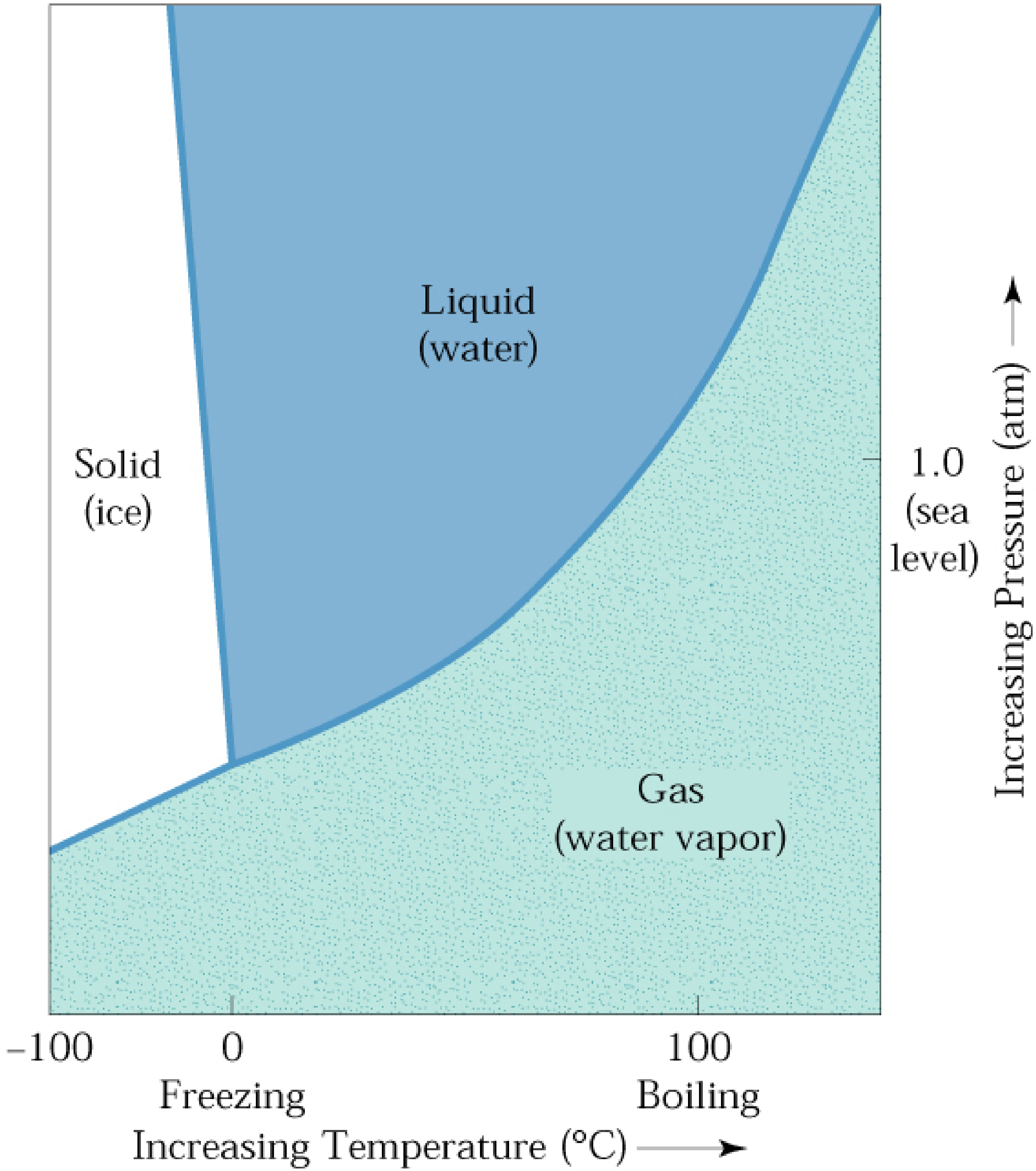
Autodissociation of water important in acid-base chemistry, many geological and biological processes

Water Properties

Low Compressibility

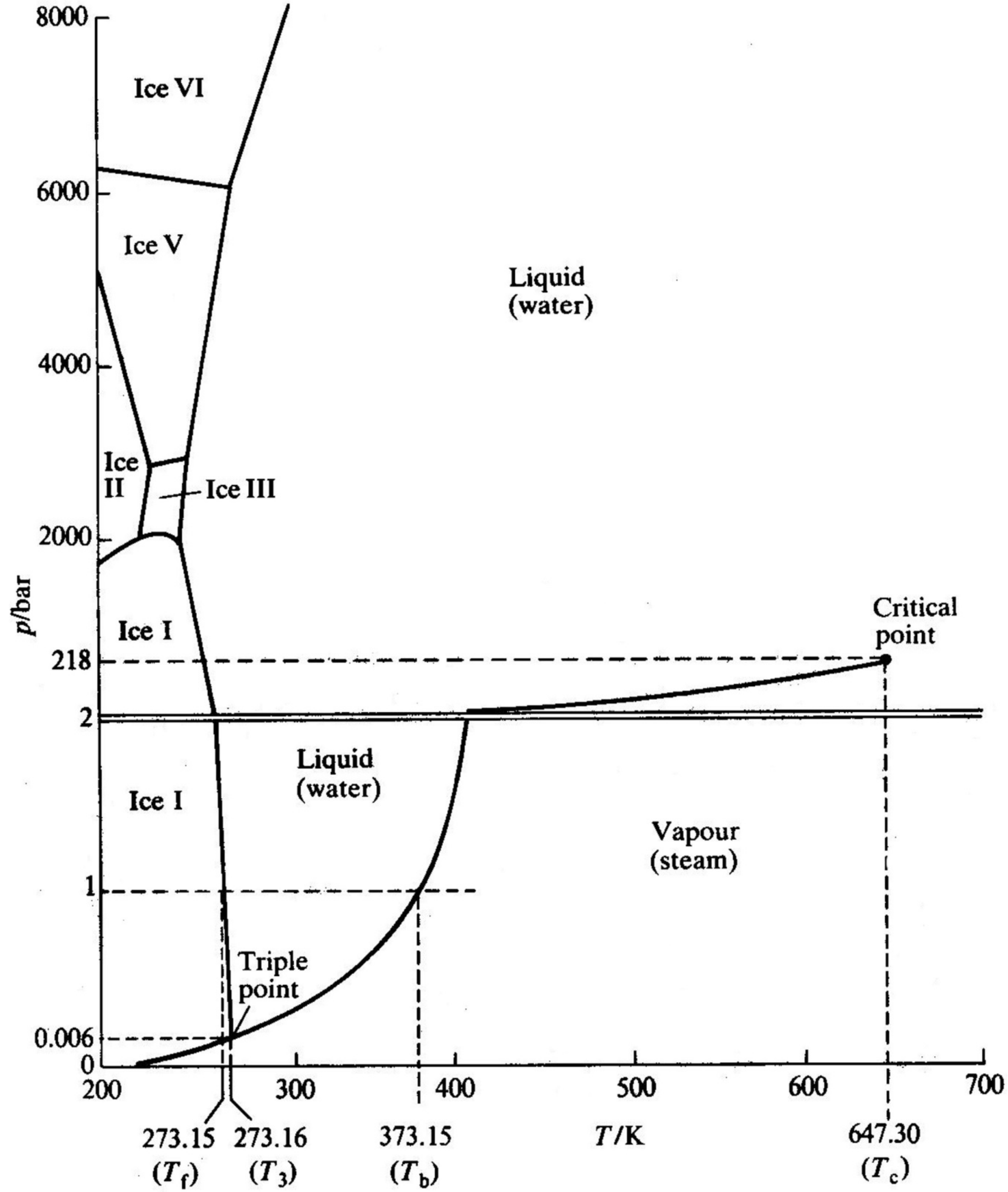
(similar to solids)

Little change in density as pressure increases with depth



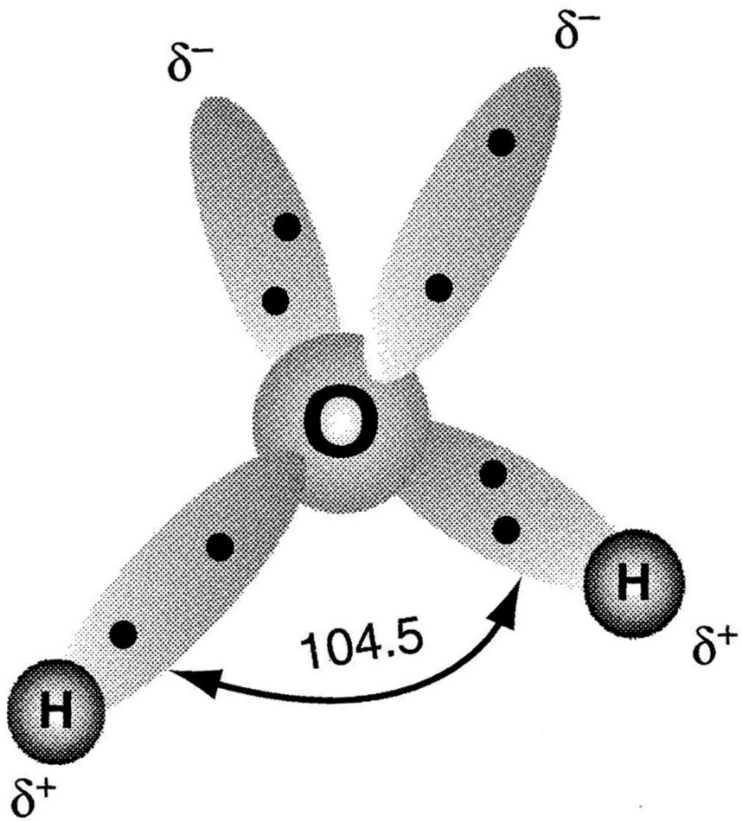
Simple Phase Diagram of Water

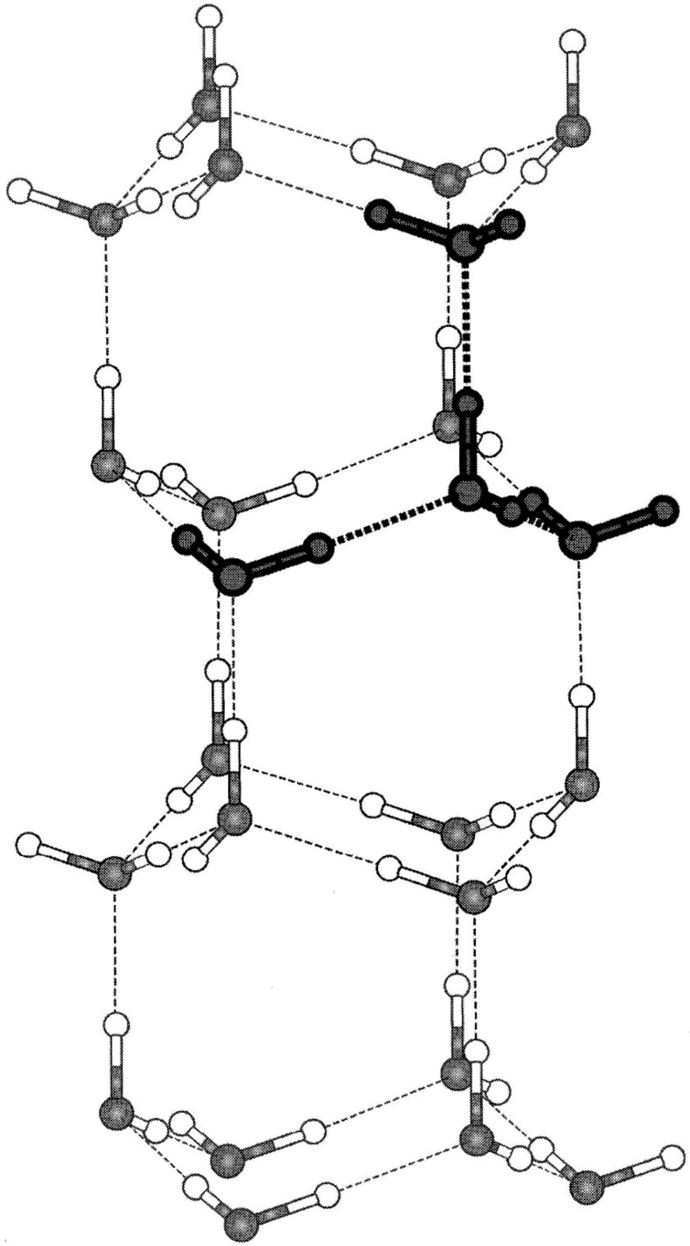
(Wiley 1999)



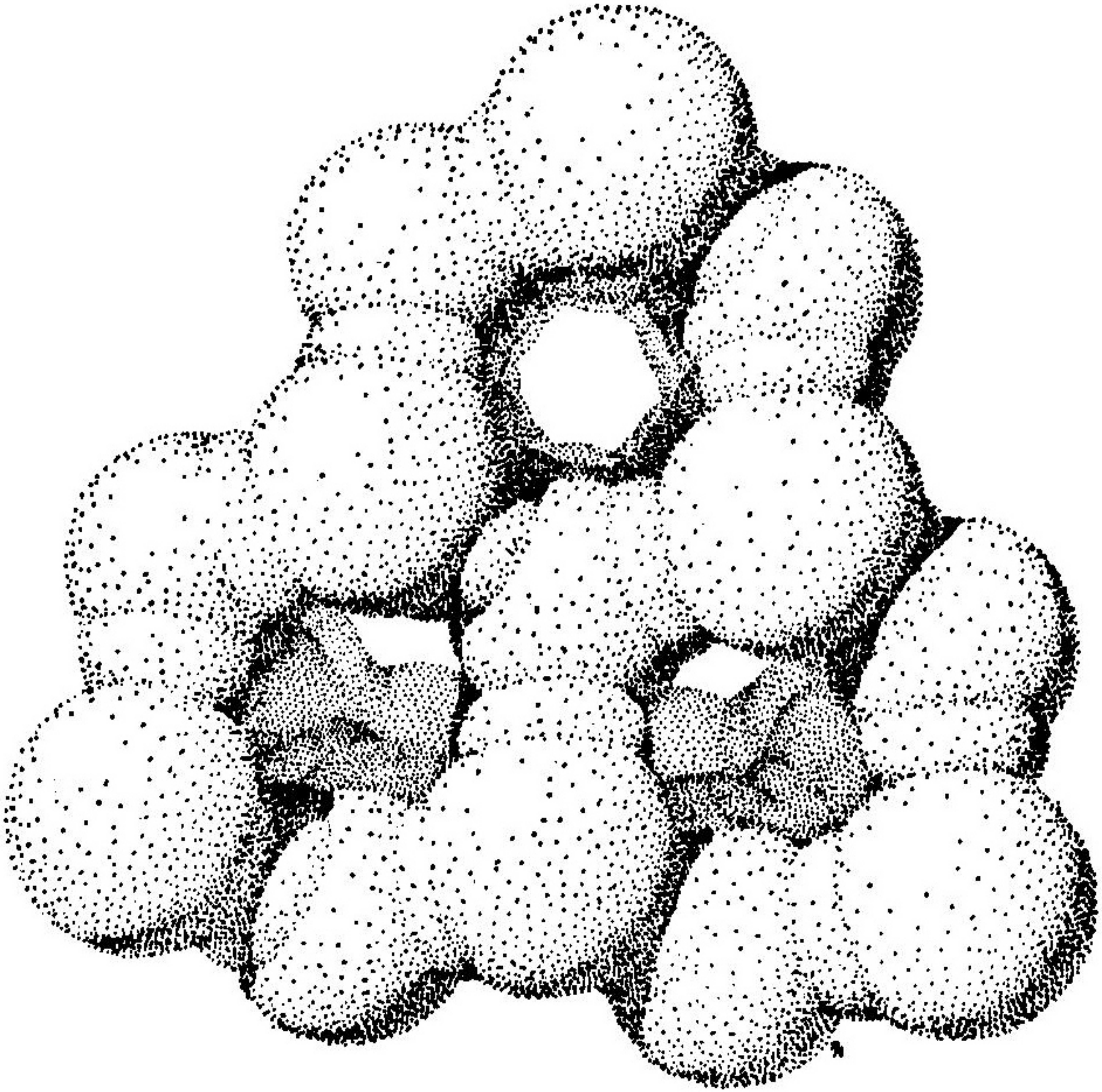
Detailed Phase Diagram of Water Showing Forms of Ice

(Atkins 1990)


δ⁻
δ⁻
O
H
H
104.5
δ⁺
δ⁺



Structure of Ice 1h with water pentamer highlighted (Emerson & Hedges Fig 3.4, page 67)

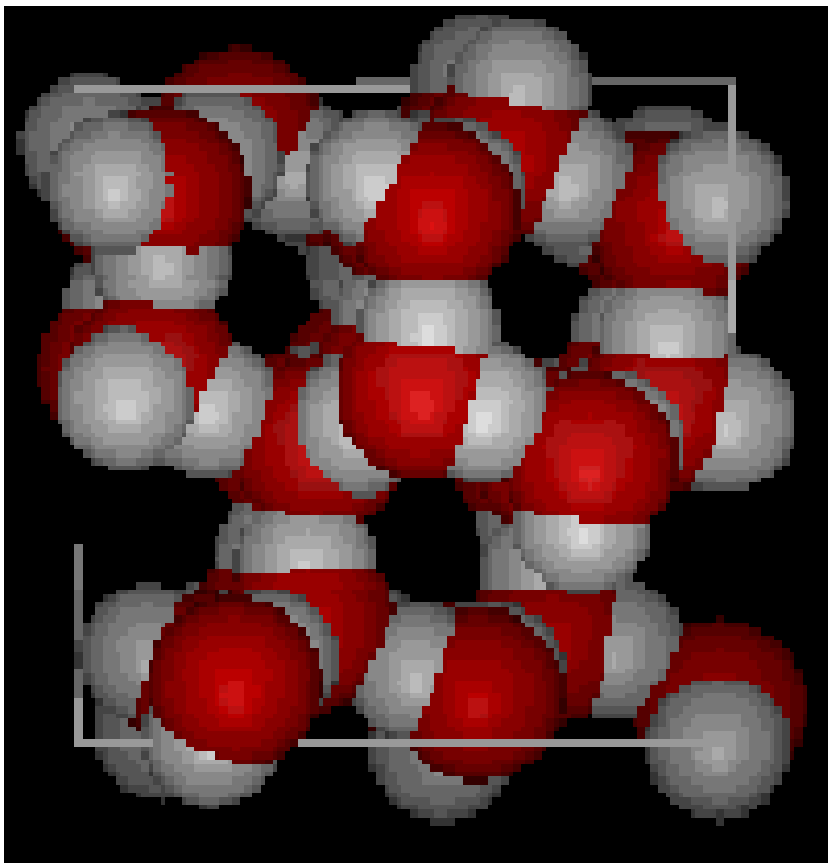


Structure of Ice 1h, Hexagonal with Space Giving Low Density

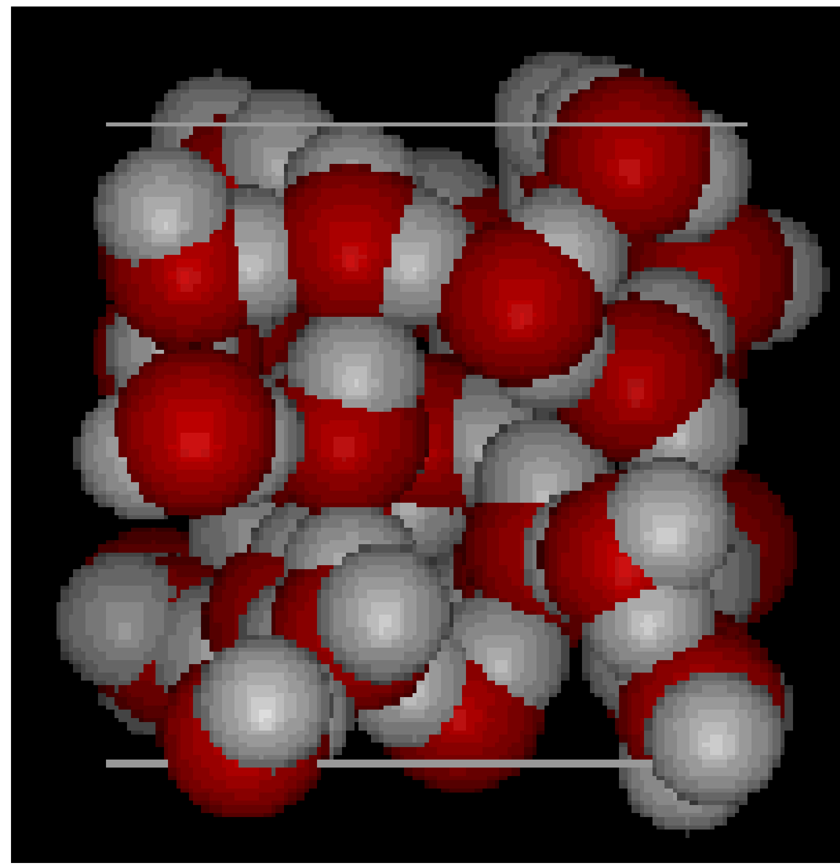
(Pilson 1998)

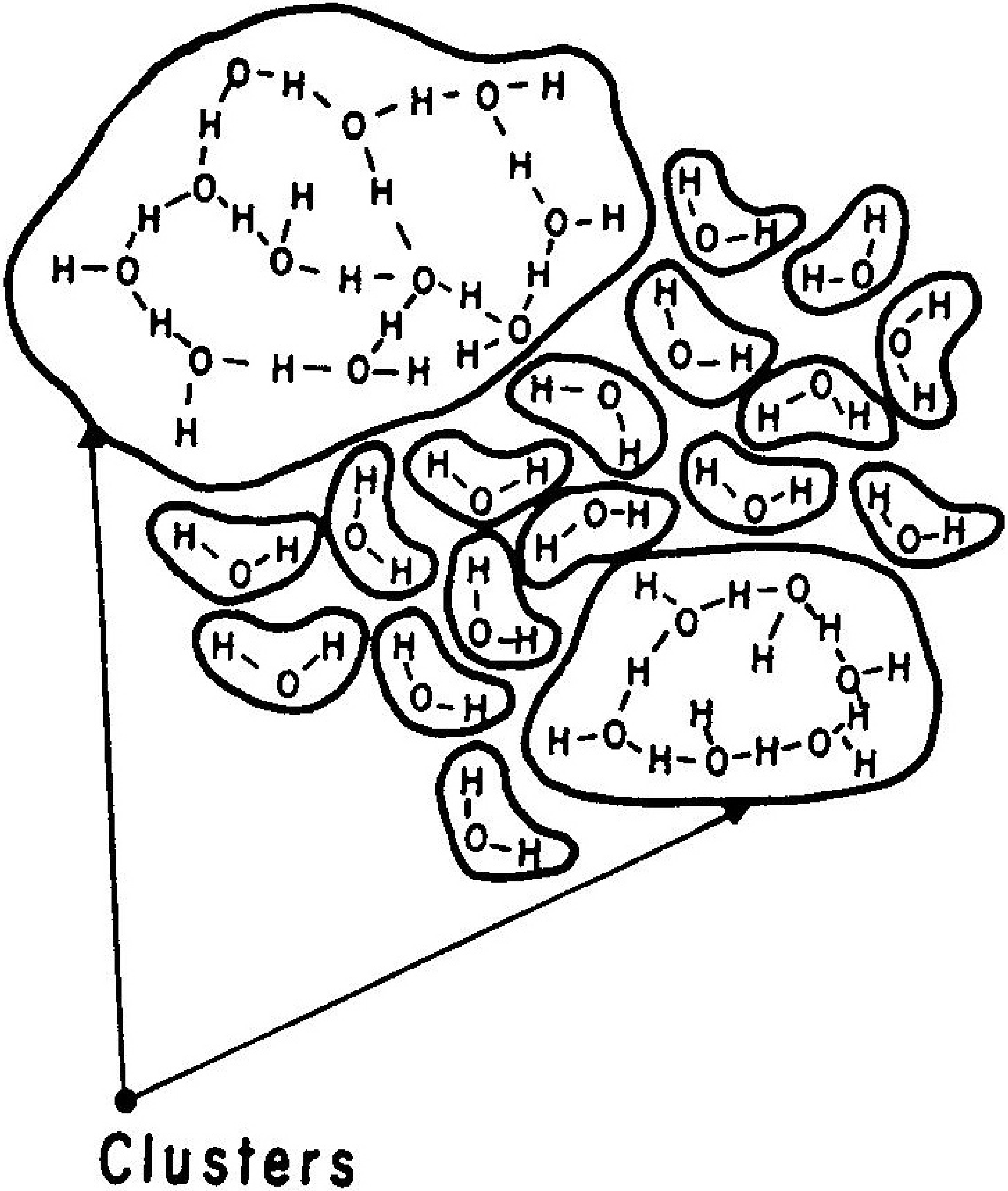
Comparison of Ice and Liquid Water Structures (NYU-SVL)

Ice 1h



Liquid Water

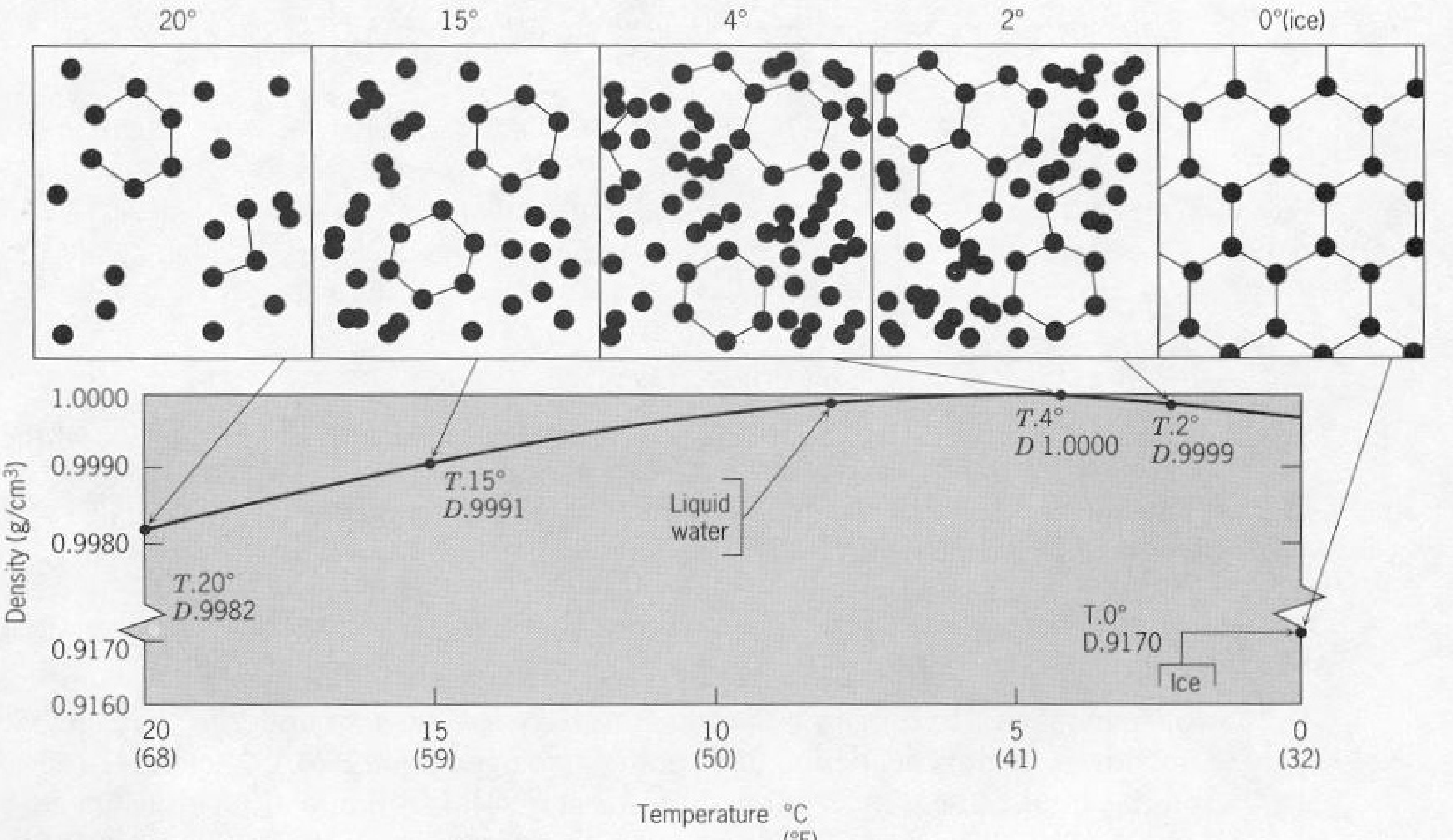




Water Clusters Dynamically Form, Break and Re-form

(Millero 2006)

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.”

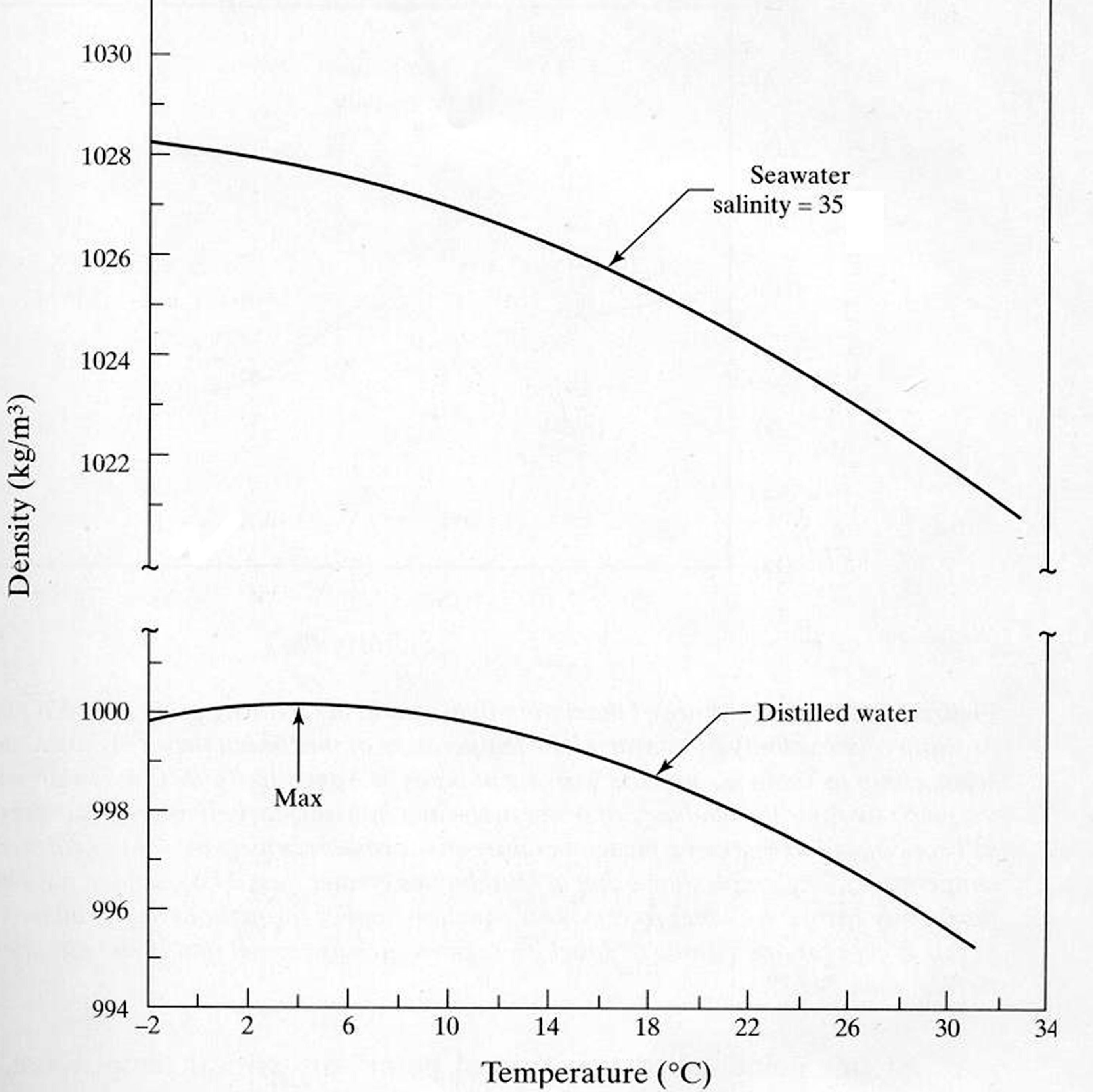
The Rime of the Ancient Mariner

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)



Temperature Density Diagram for Pure Water & Seawater Salinity of 35

(Pilson 1998)

TABLE 2.2

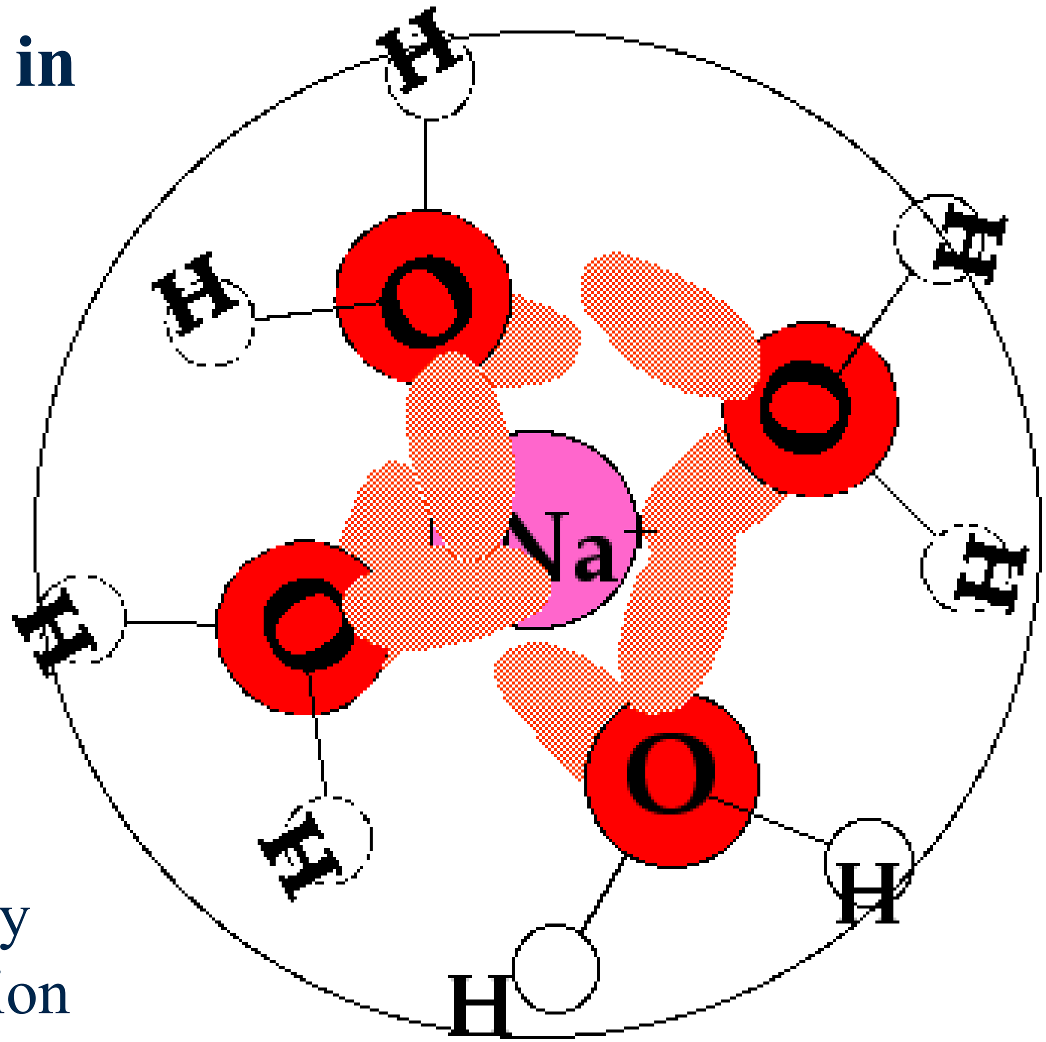
Comparison of Pure Water and Seawater Properties

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, $J\ g^{-1}\,°C^{-1}$	3.898	4.182

Source: From *Marine Chemistry*, R. A. Horne, copyright © 1969 by John Wiley & Sons, Inc., New York, p. 57. Reprinted with permission.

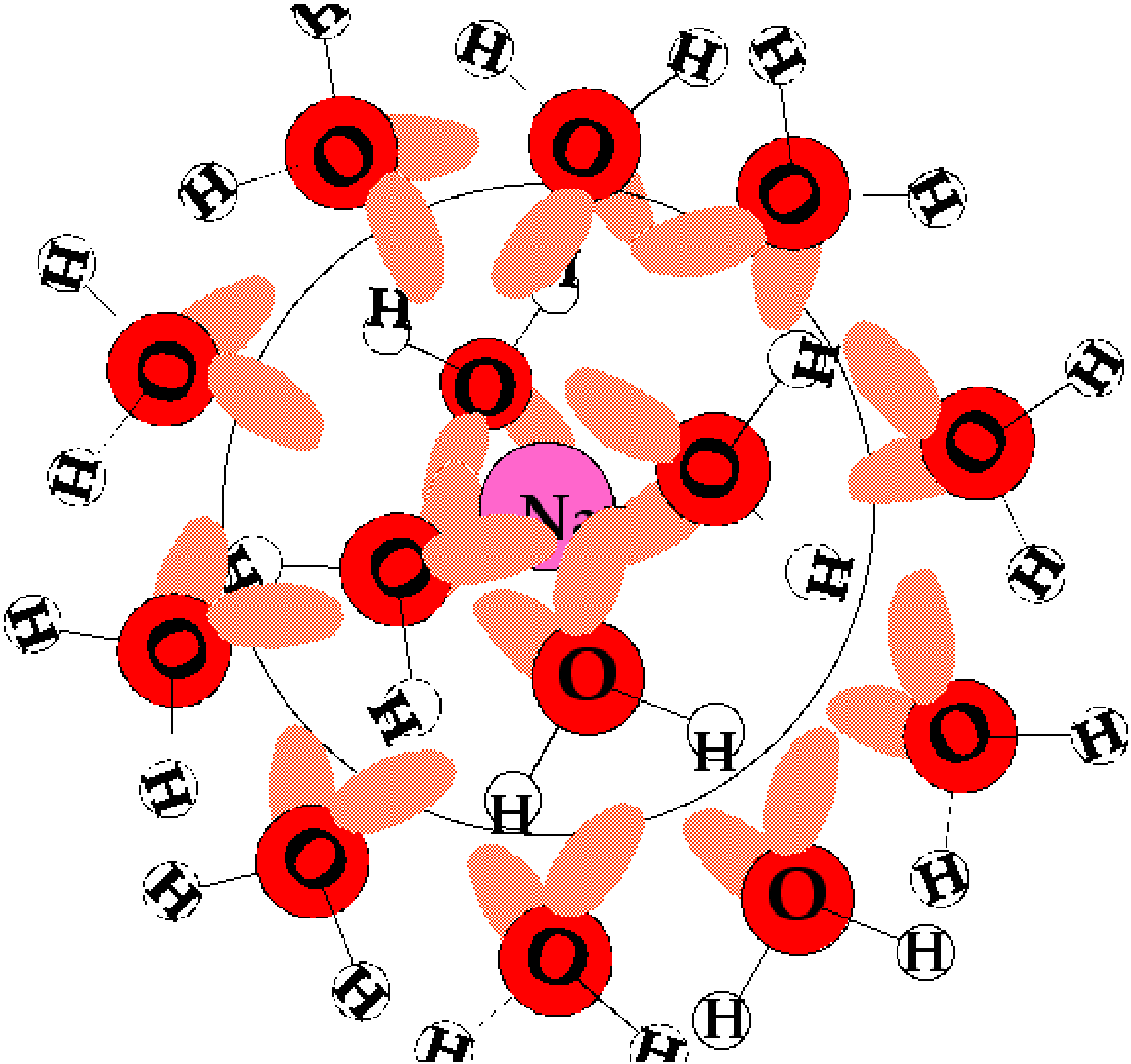
Some Properties Undergo Dramatic Changes

Adding an Ion Like Sodium (Na^+) Changes Some Things in H_2O



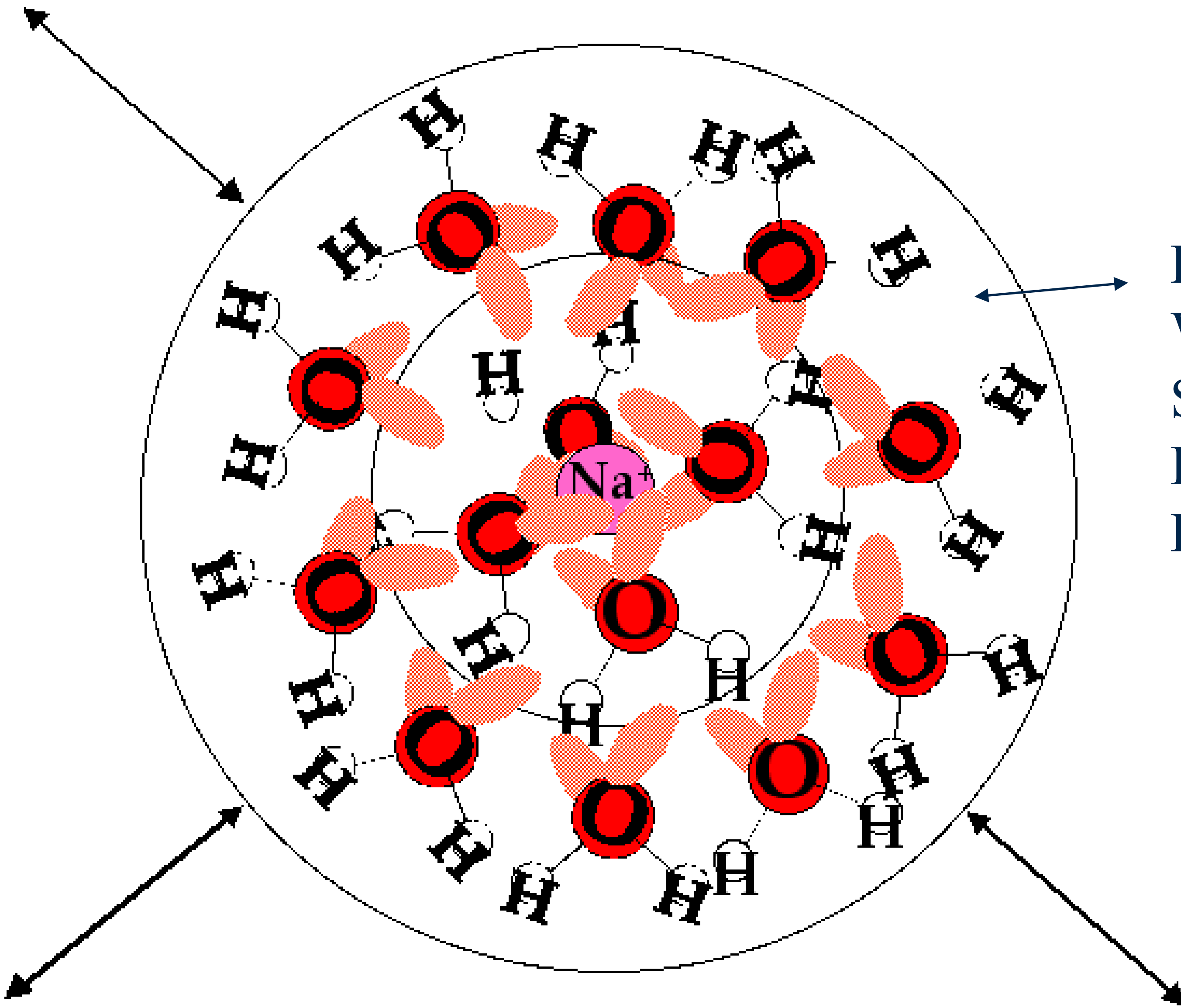
Primary Solvation Shell of H_2O

Polarity, High Dielectric Constant Result in Strong Solvation or Hydration of Na^+ by H_2O



Secondary Solvation Shell or a Second Sphere of H_2O is Bound to the First

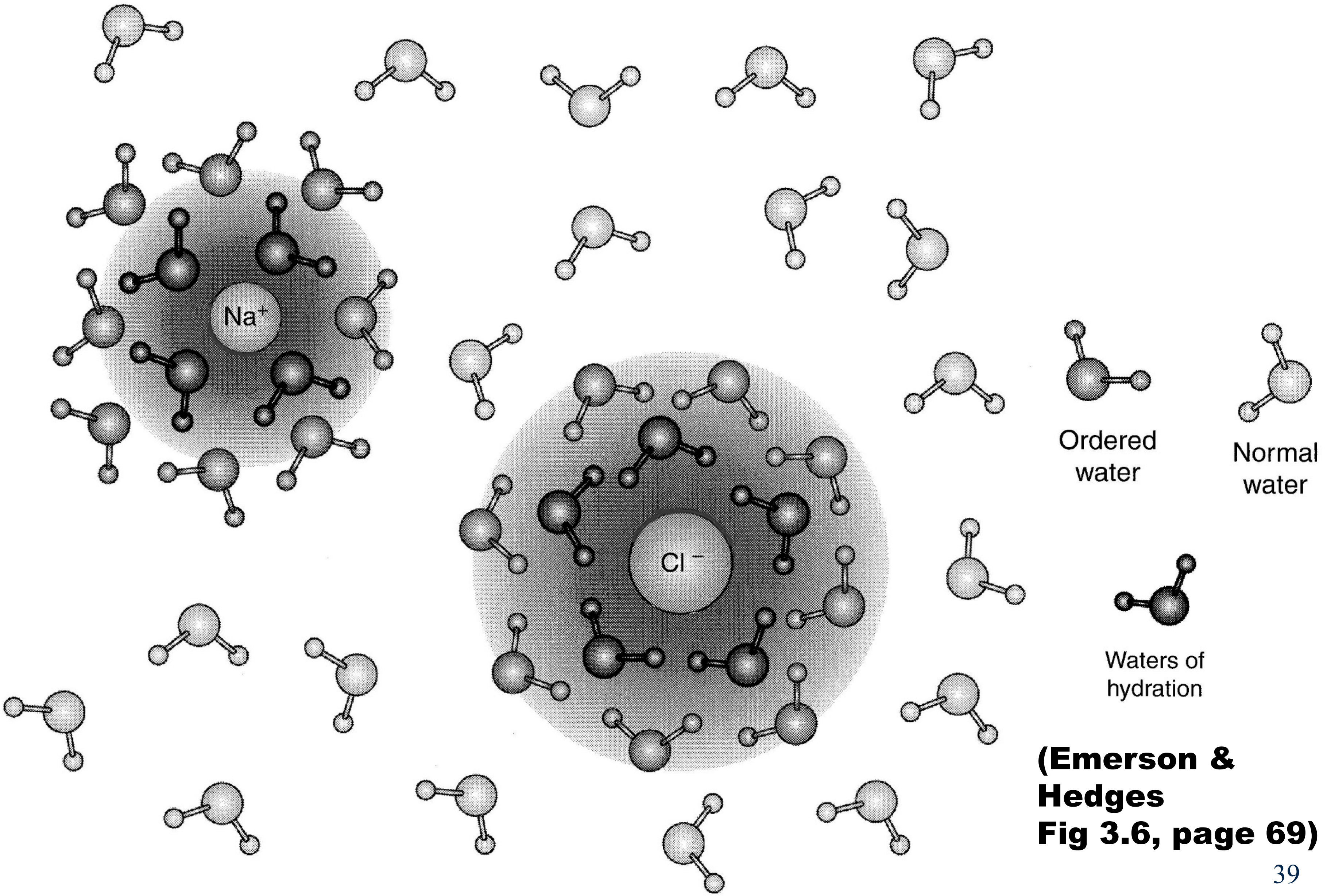
Normal H_2O Structure Exists
Out Here for "Bulk" Water



Disrupted
Water
Structure
Exists in
Here

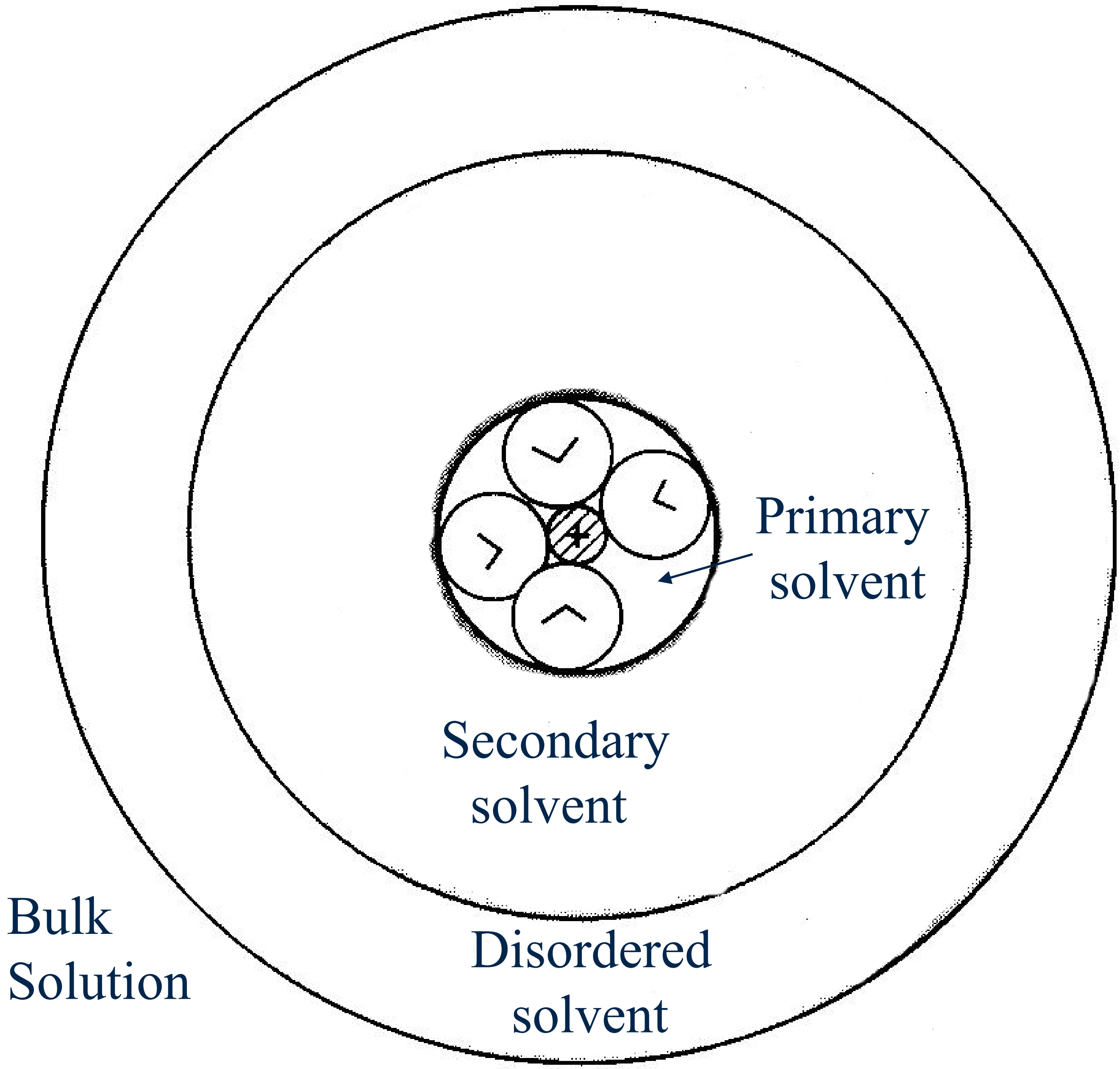
Bulk Water

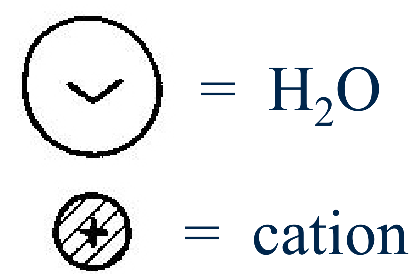
Bulk Water

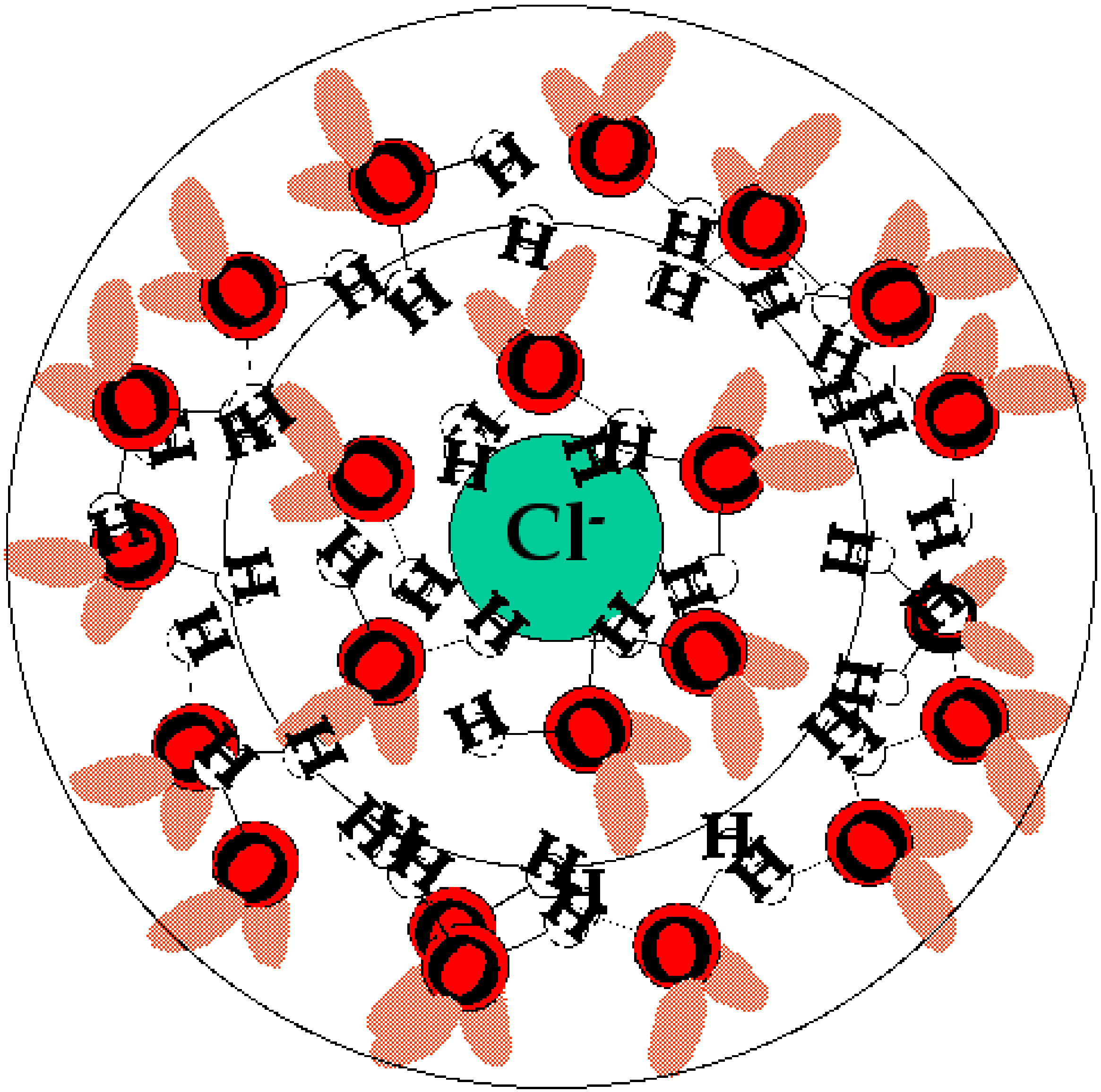


(Emerson & Hedges Fig 3.6, page 69)

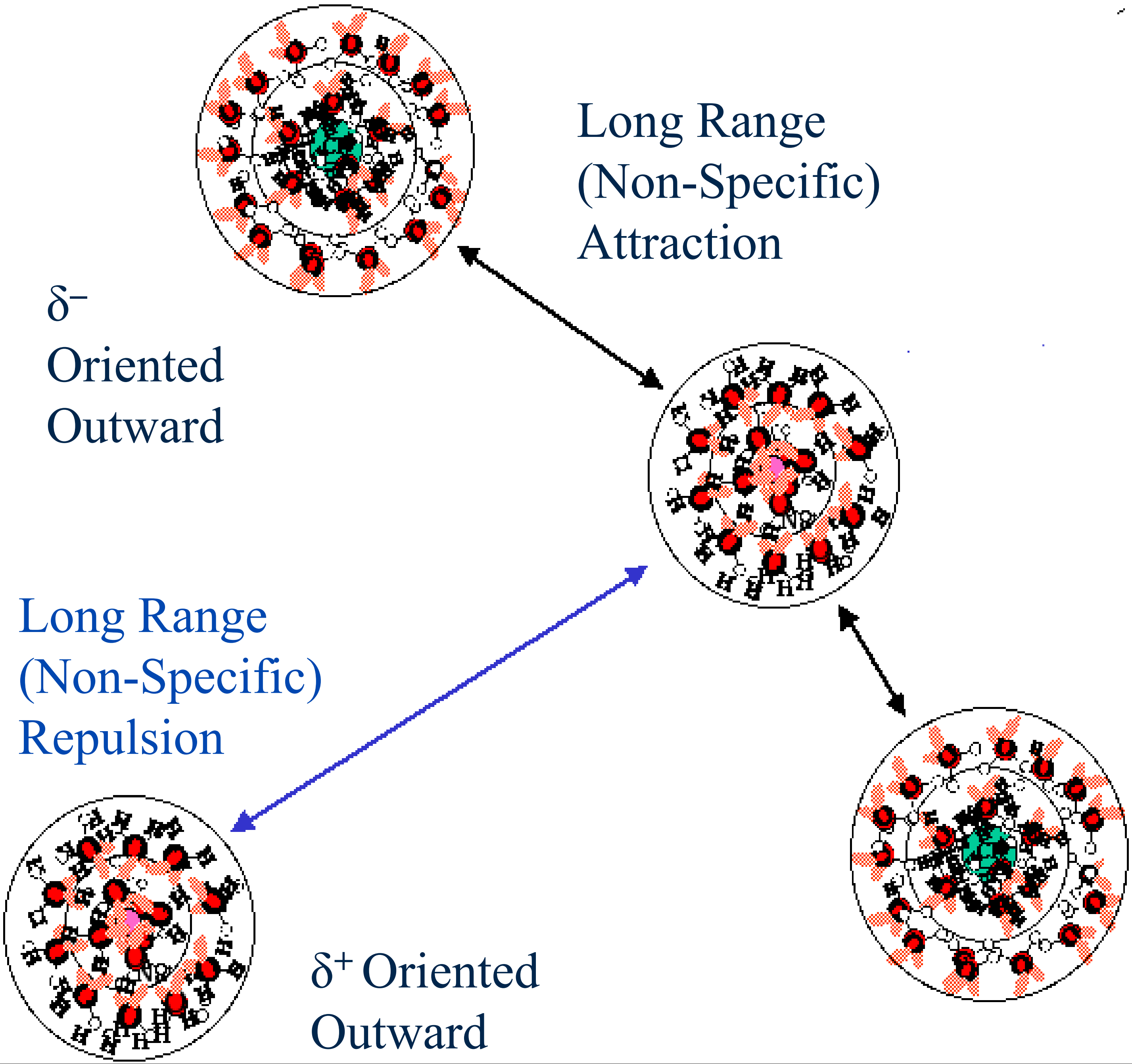
Hydrated Ion (Morel 1993)







For Anions the Concept is Analogous Only Reversed With Respect to the Orientation of the H_2O



Other Effects Also Occur