Chemical Oceanography

Dr. David K. Ryan
Department of Chemistry
University of Massachusetts Lowell
&
Intercampus Graduate School
of Marine Sciences and Technology

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

Water – Amazing Stuff

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 details or guarantee availability.

Website for Millero 1996 & Periodic Tables

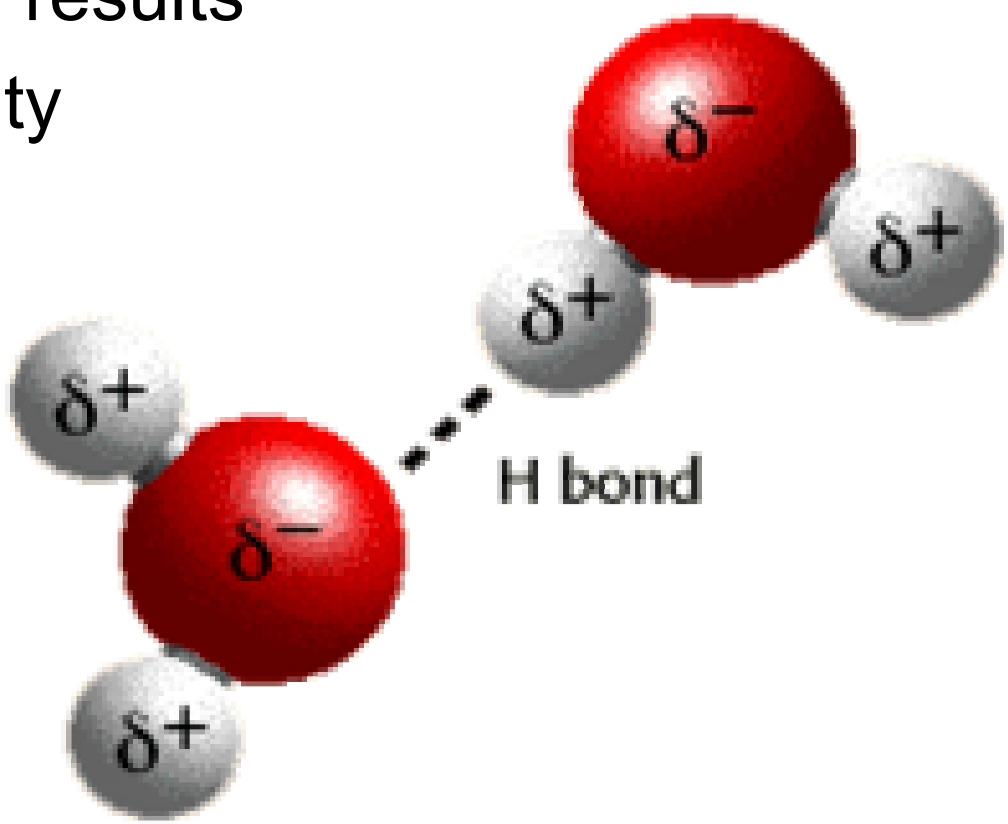
http://fig.cox.miami.edu/~lfarmer/MSC215/MSC215.HTM

www.mbari.org/chemsensor/pteo.htm

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

Hydrogen Bonding is key to anomolous properties of water

H-Bonding results from polarity



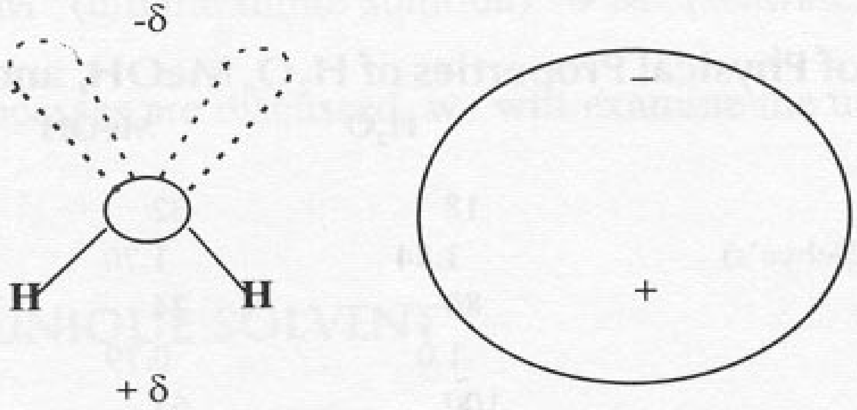


FIGURE 4.3. The water dipole.

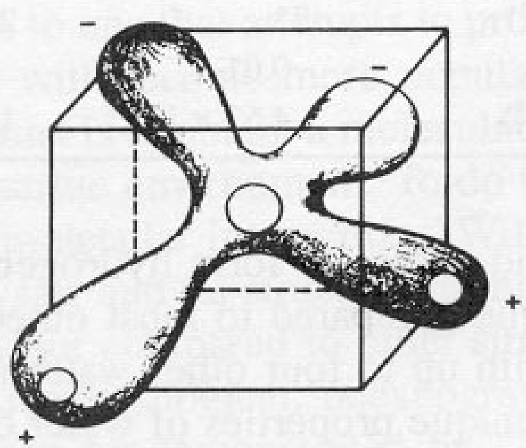
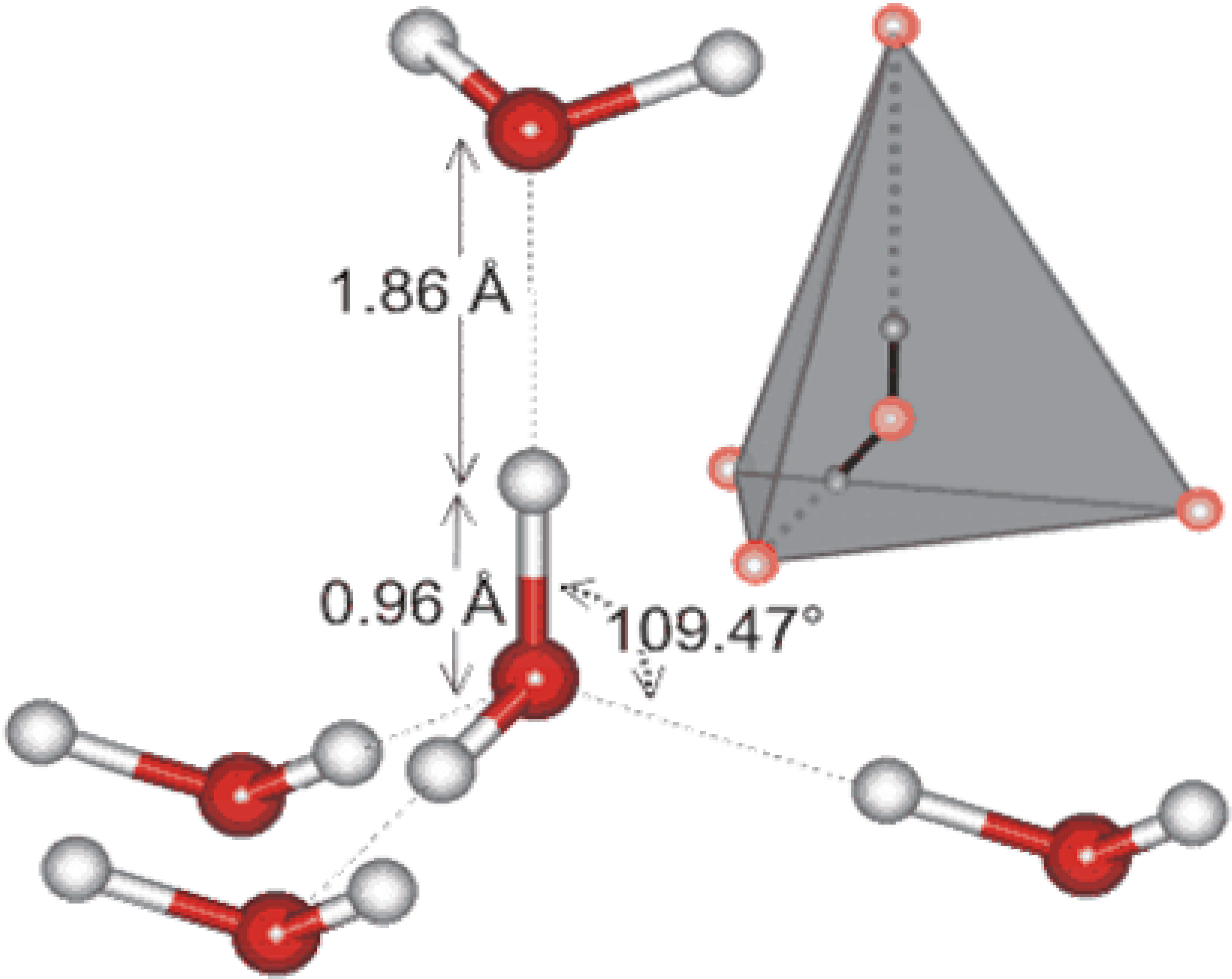


FIGURE 4.4. The three-dimensional structure of the water molecule.

Dipole & Quadrapole Diagrams (Millero)

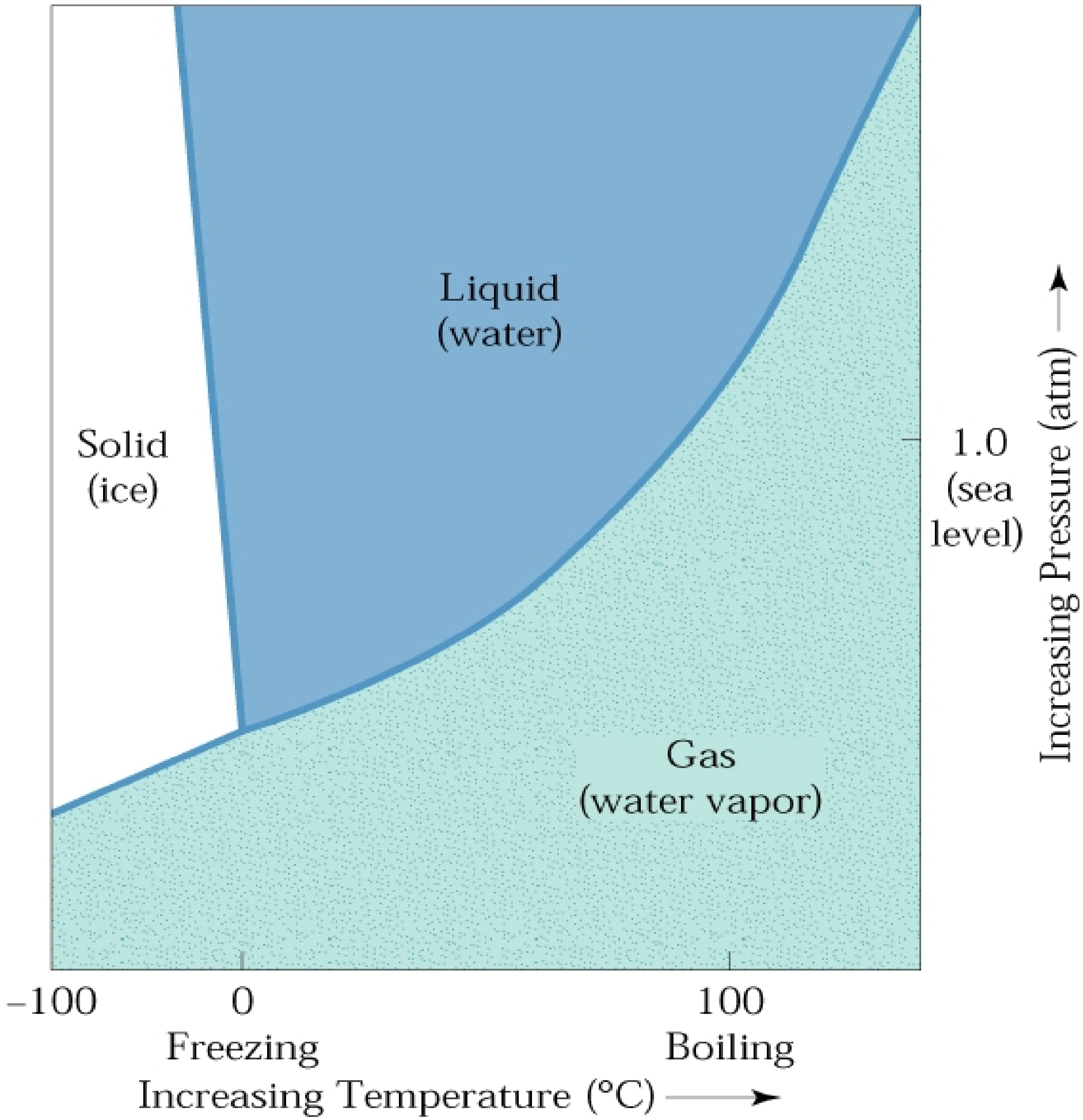


Arrangement for Hydrogen Bonding - Pentamer

Millero

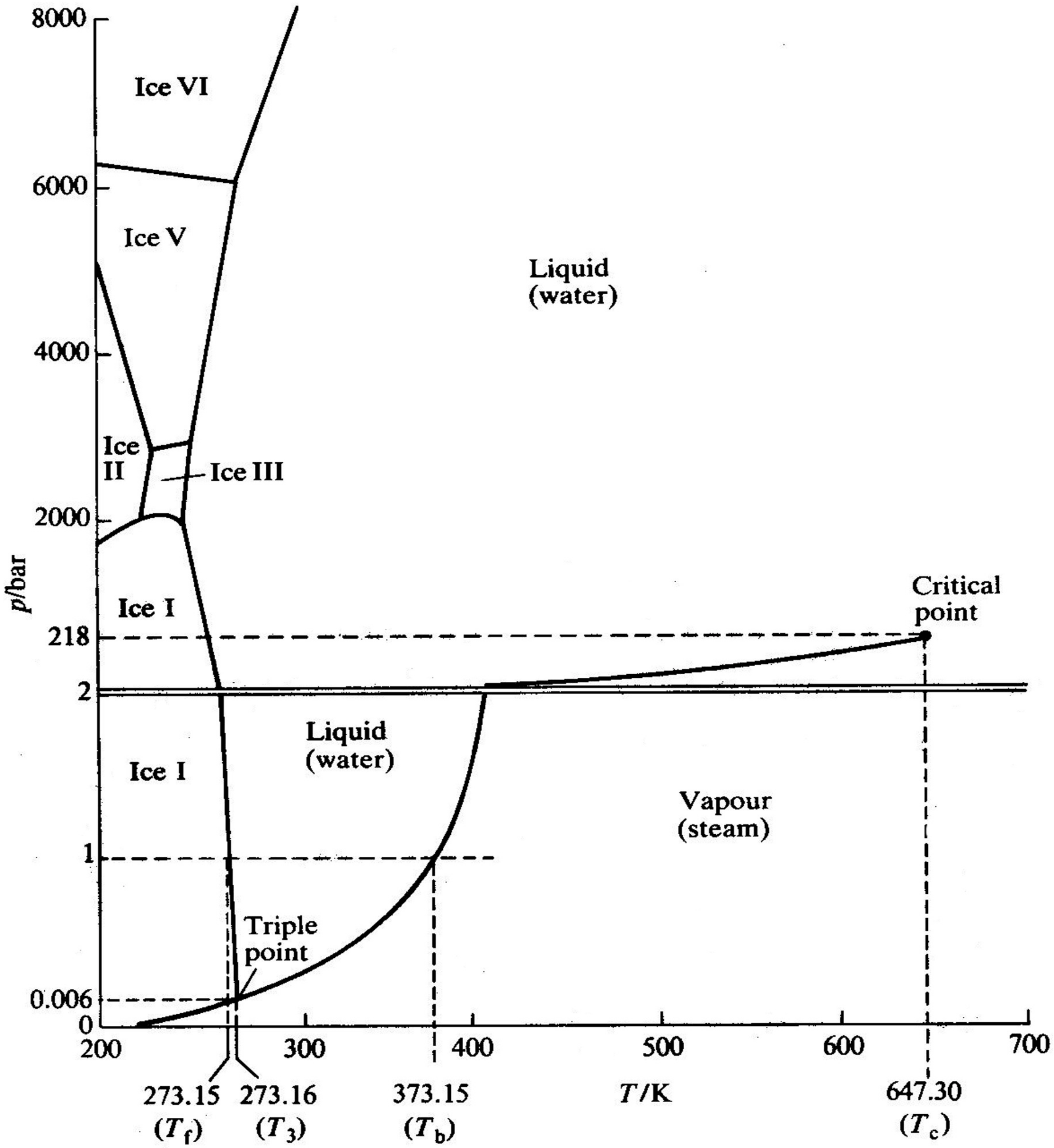
TABLE 4.1
Comparison of Physical Properties of H_2O, MeOH, and n-Heptane

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}



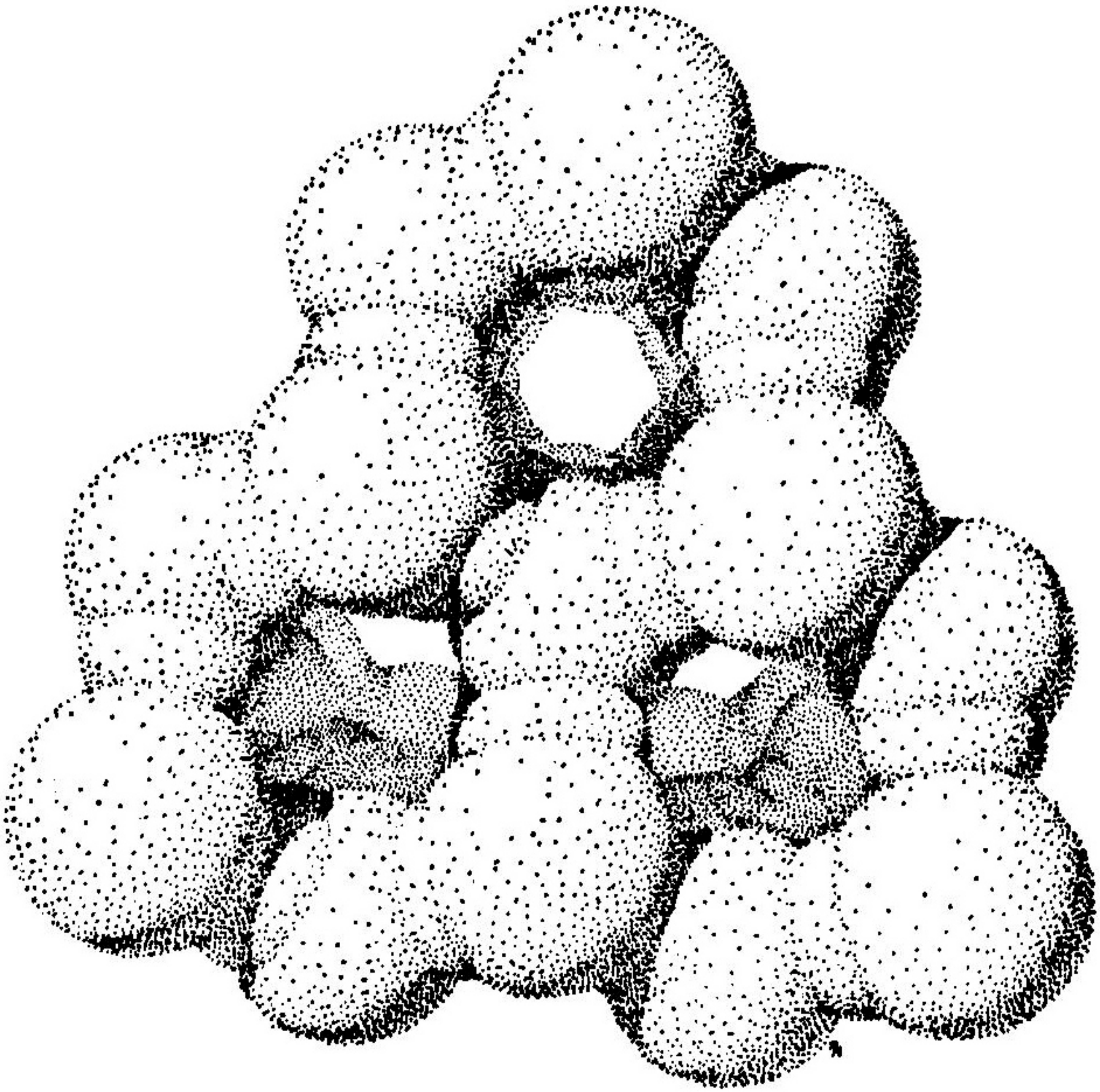
Simple Phase Diagram of Water

(Wiley 1999)



Detailed Phase Diagram of Water Showing Forms of Ice

(Atkins 1990)

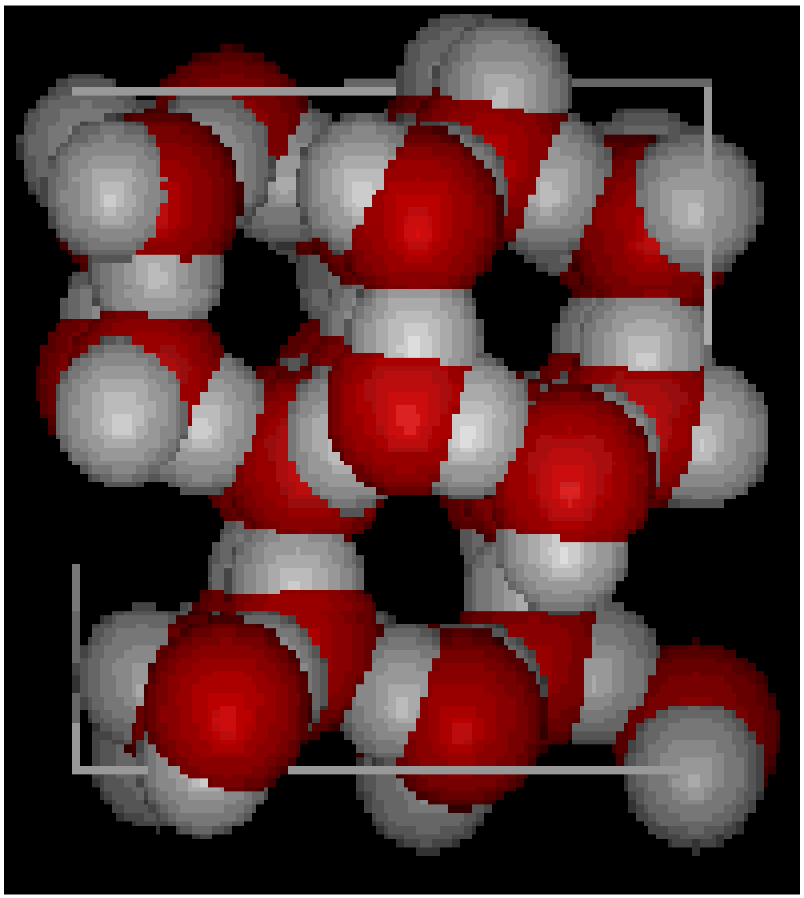


Structure of Ice 1h, Hexagonal with Space Giving Low Density

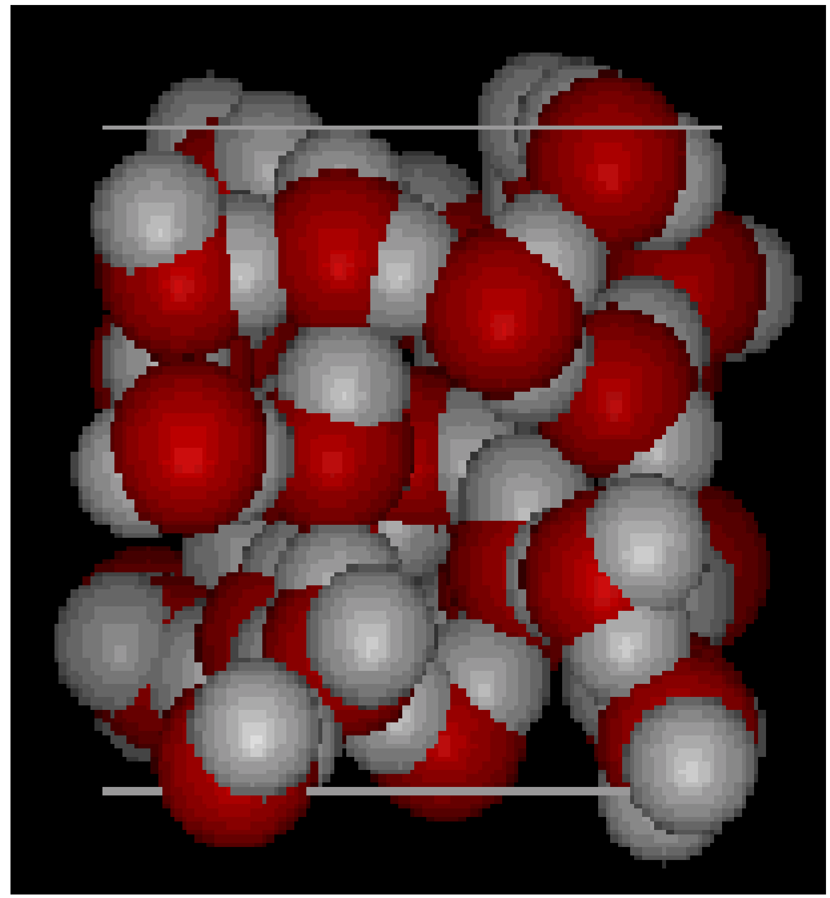
(Pilson 1998)

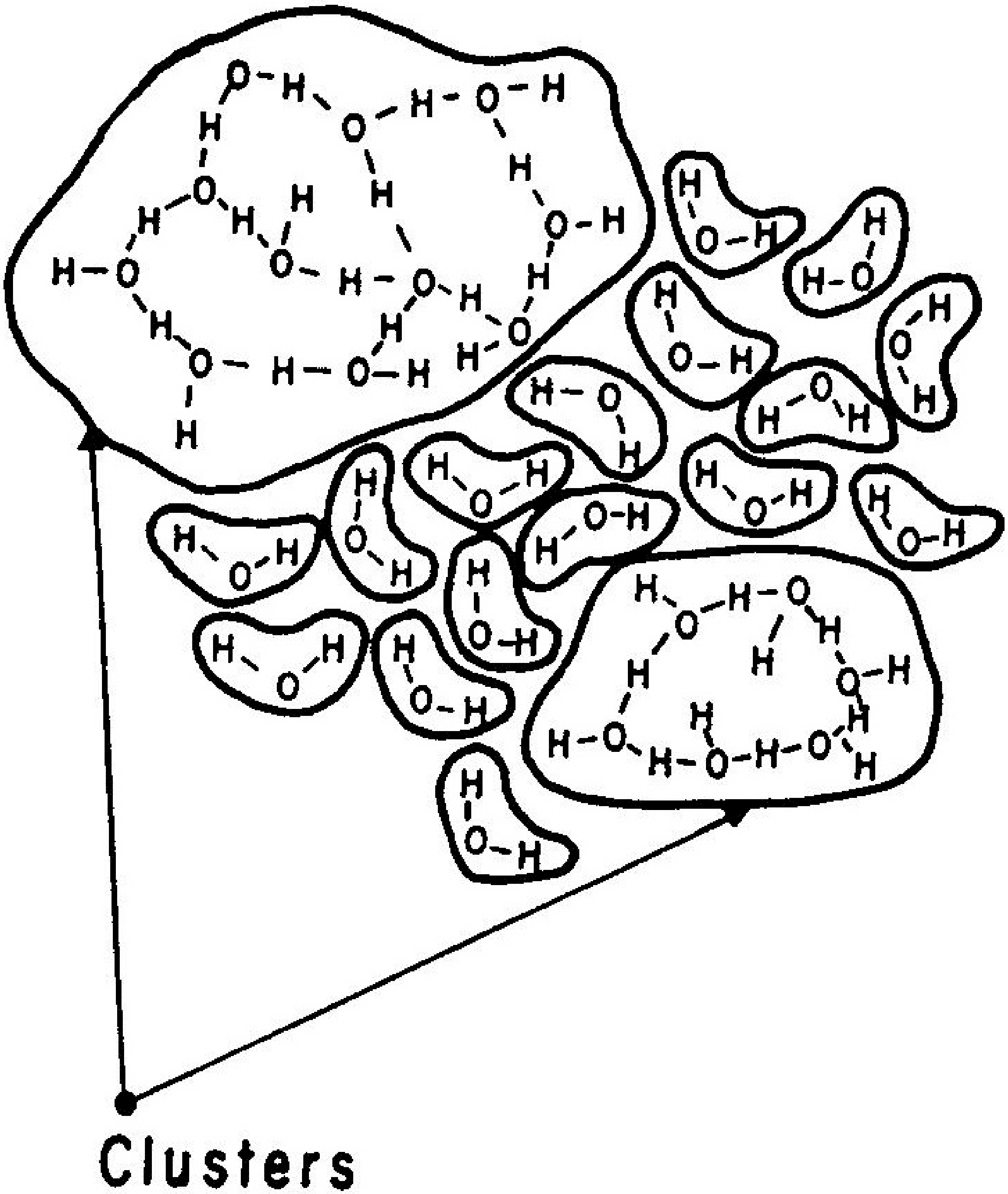
Comparison of Ice and Liquid Water Structures (NYU-SVL)

Ice 1h



Liquid Water

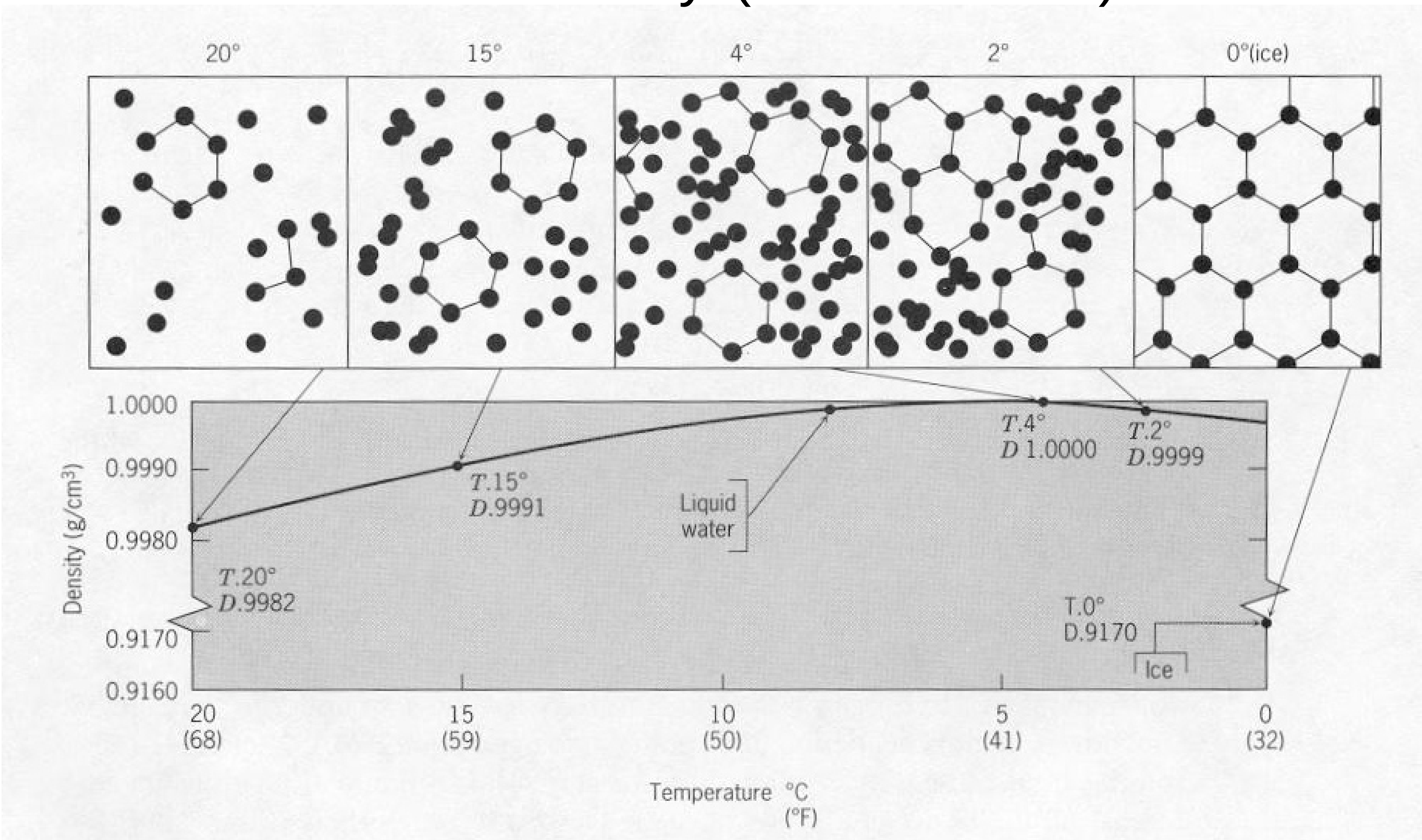




Water Clusters Dynamically Form, Break and Re-form

(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.”**

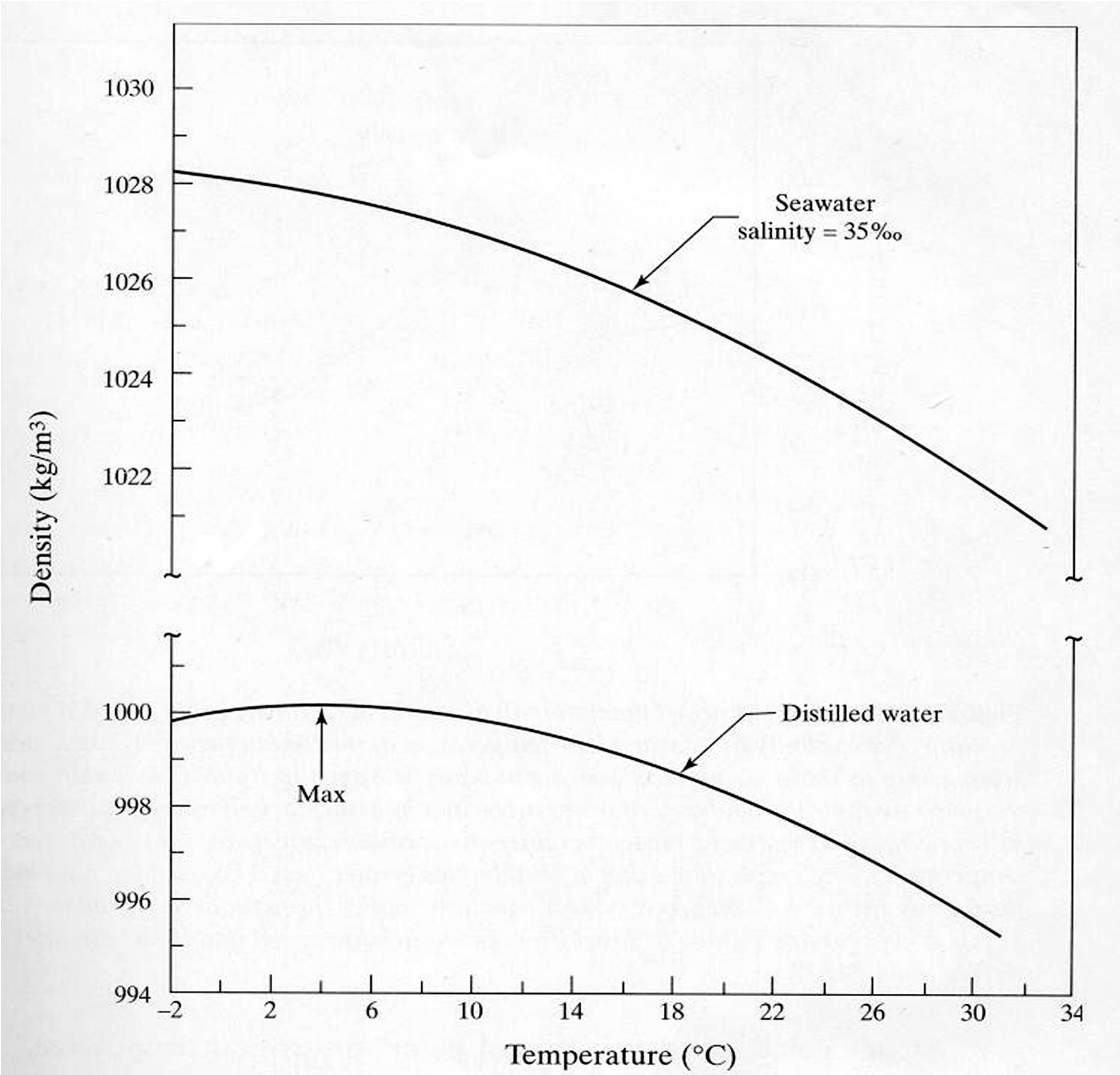
The Rime of the Ancient Mariner

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 Chemistry of H_2O
- Millero – Ion-Water Interactions p. 134



Temperature Density Diagram for Pure Water & Seawater at 35 PSU

(Pilson 1998)

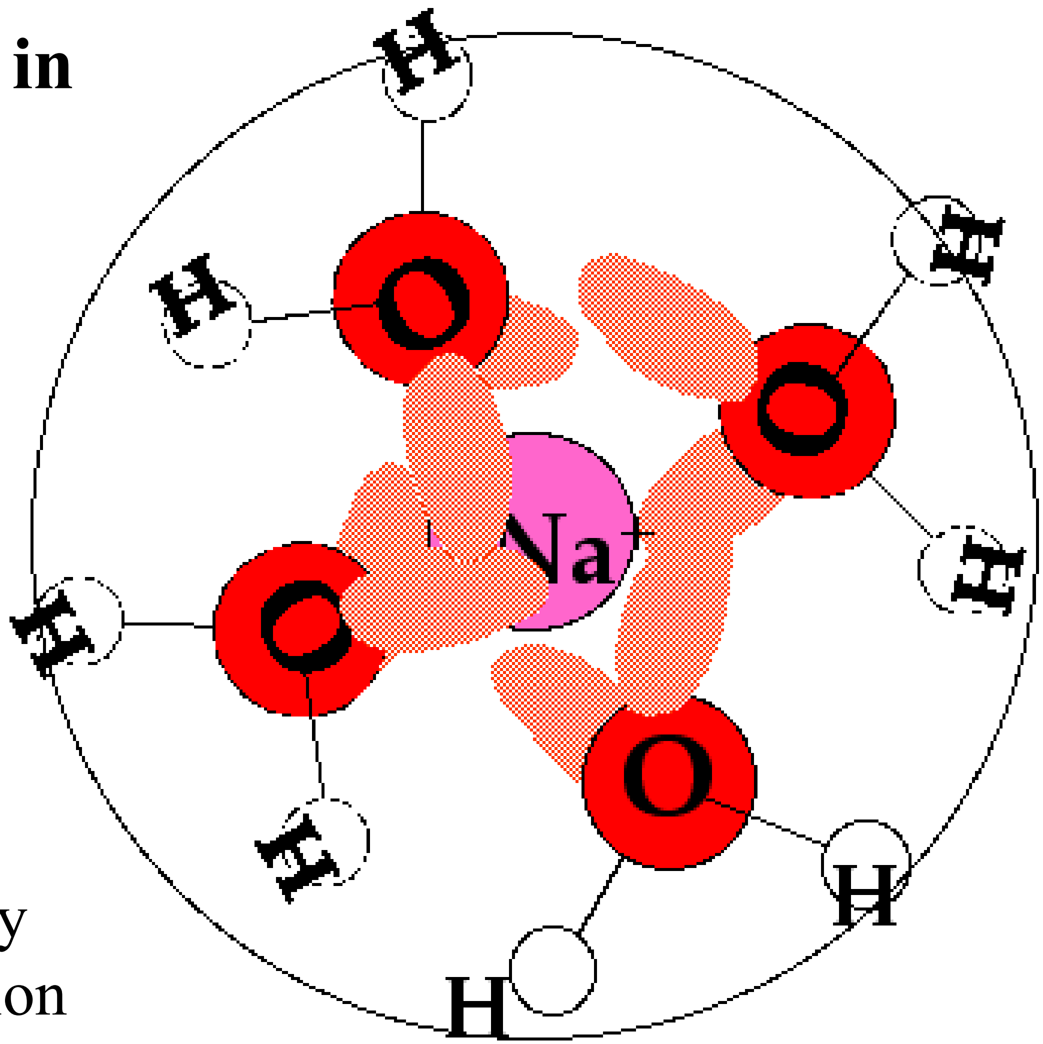
TABLE 2.2
Comparison of Pure Water and Seawater Properties

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, $J\ g^{-1}\,°C^{-1}$	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.

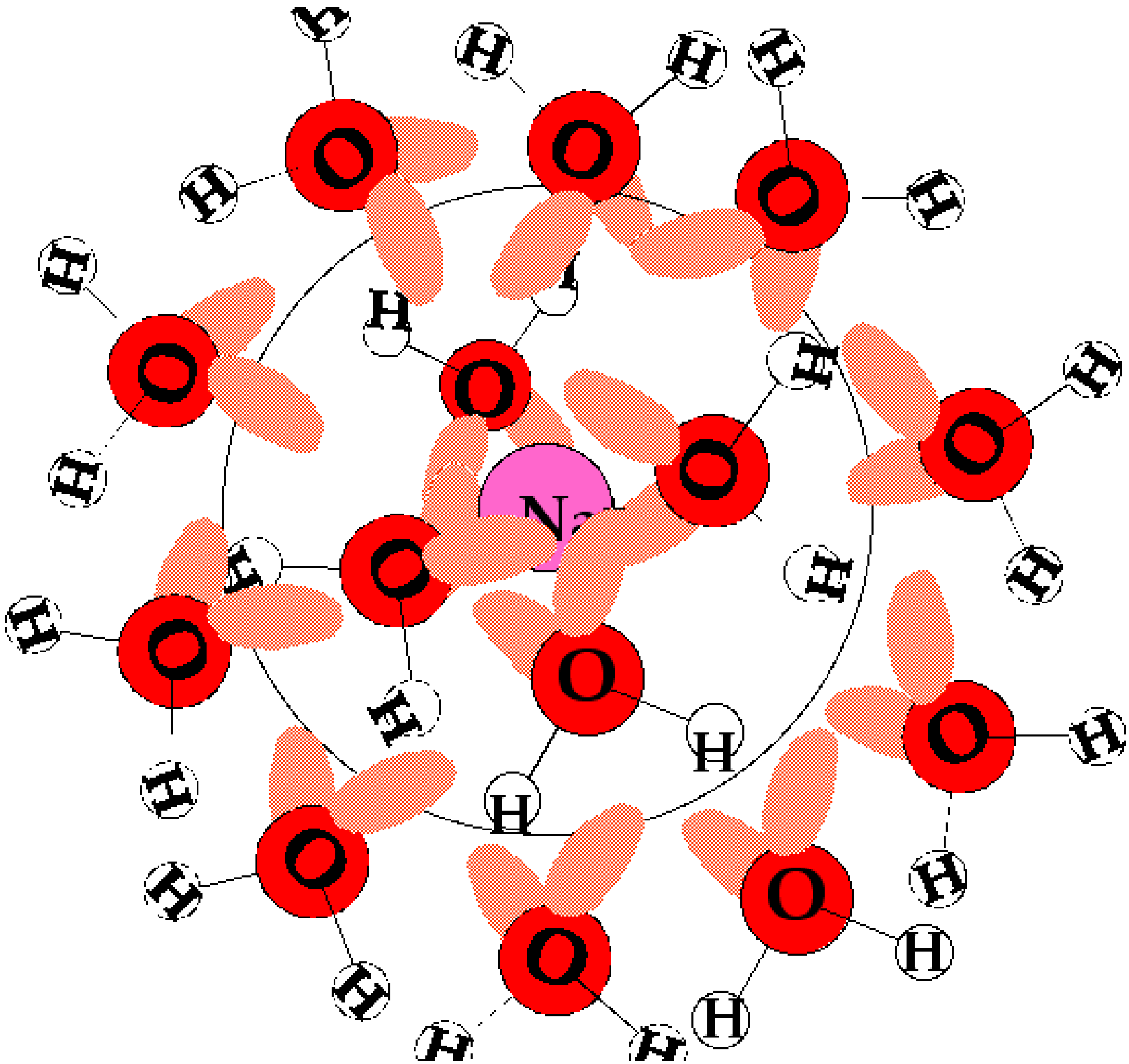
Some Properties Undergo Dramatic Changes

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



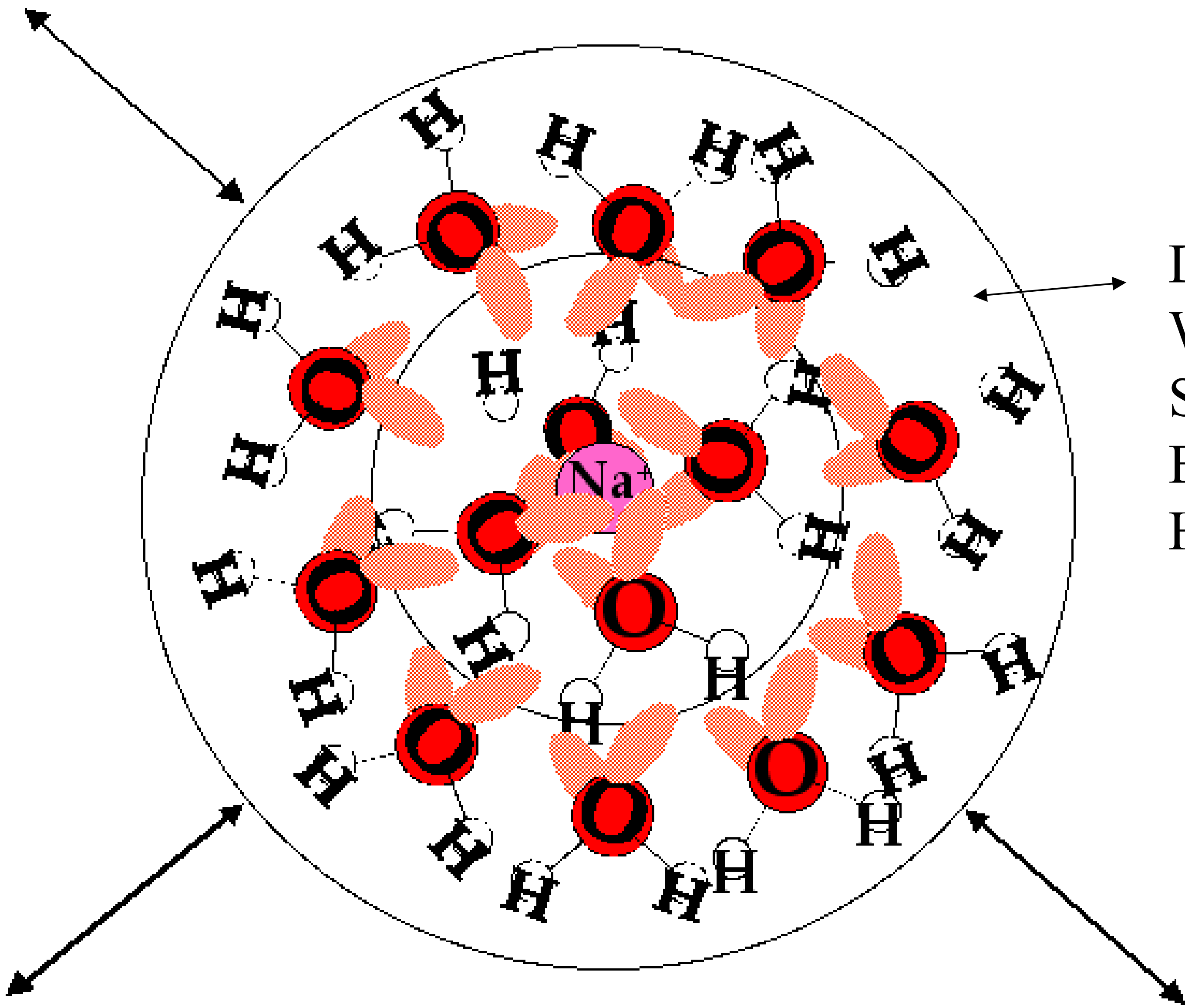
Primary Solvation Shell of H_2O

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

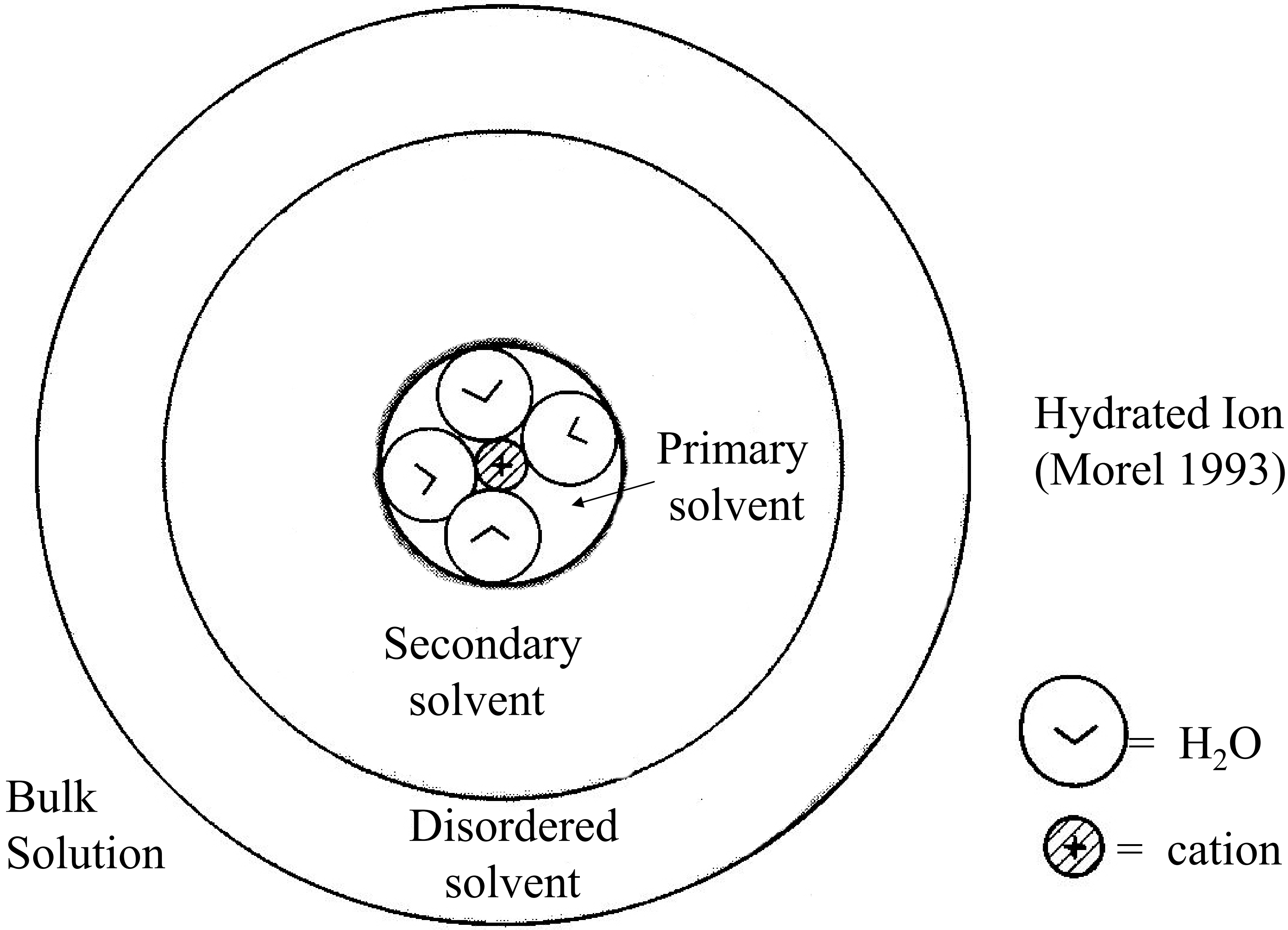
Normal H_2O Structure Exists
Out Here for “Bulk” Water

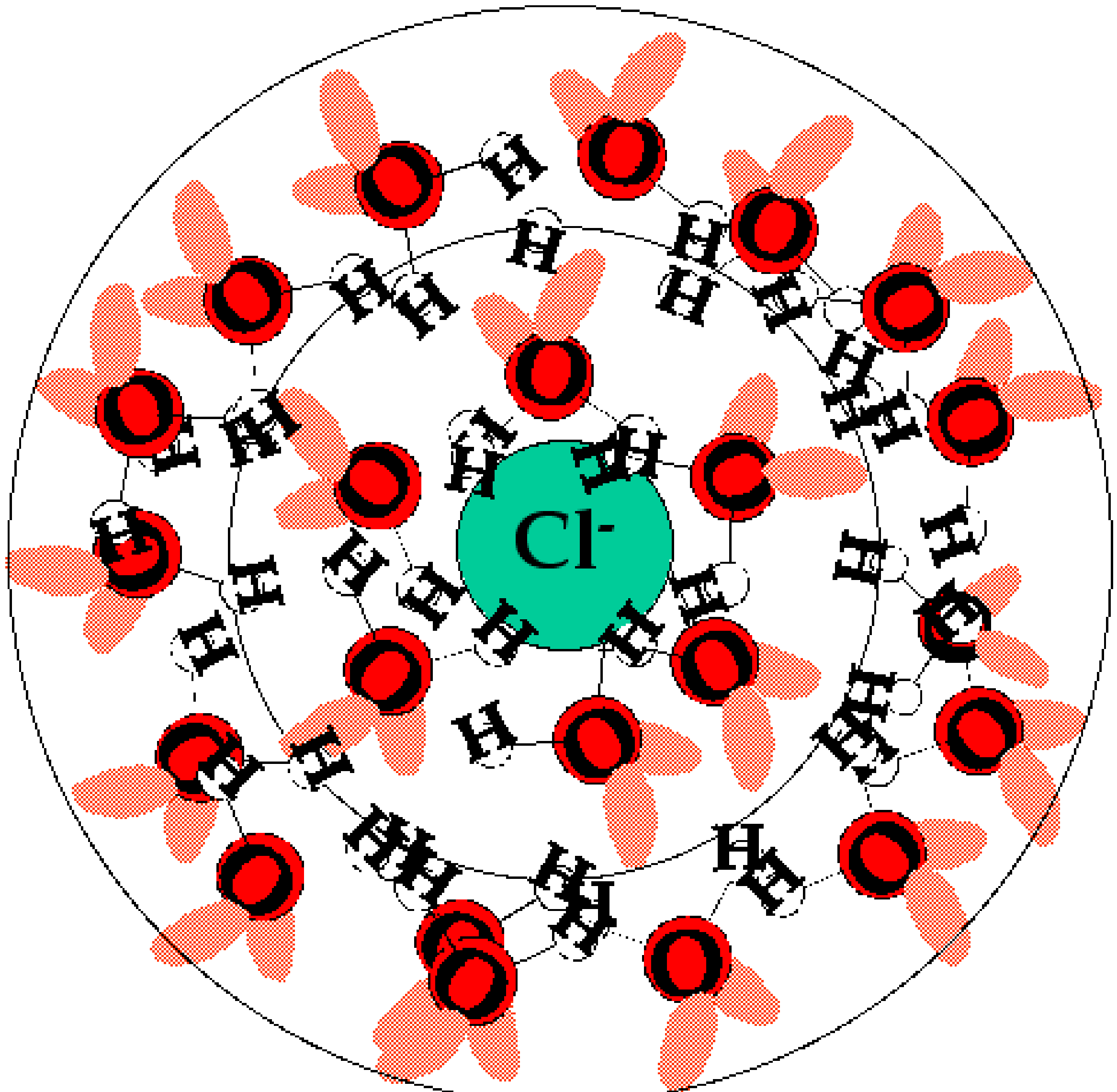


Disrupted
Water
Structure
Exists in
Here

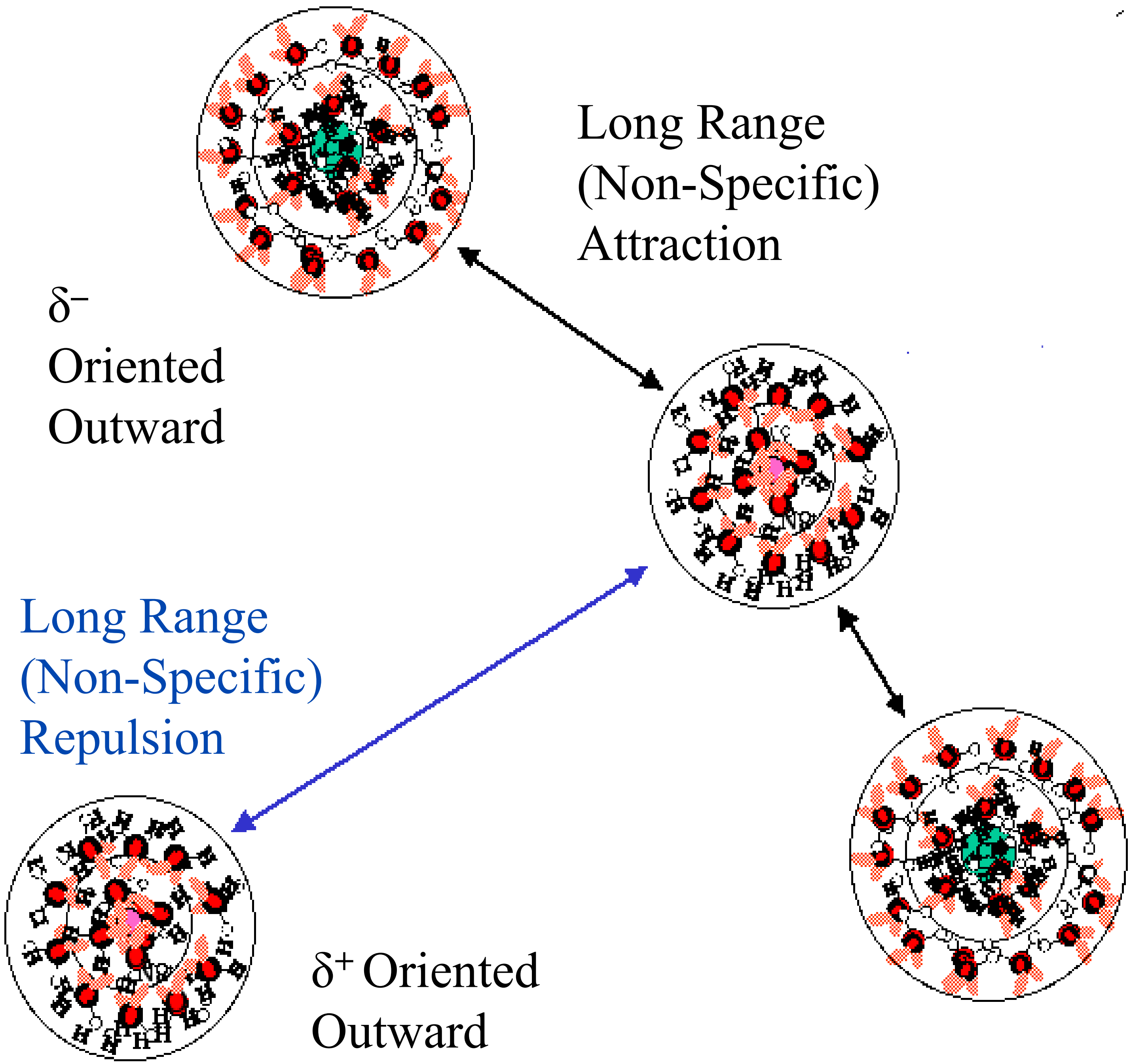
Bulk Water

Bulk Water


Hydrated Ion
(Morel 1993)
Primary
solvent
Secondary
solvent
Disordered
solvent
Bulk
Solution
= H_2O
= cation



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



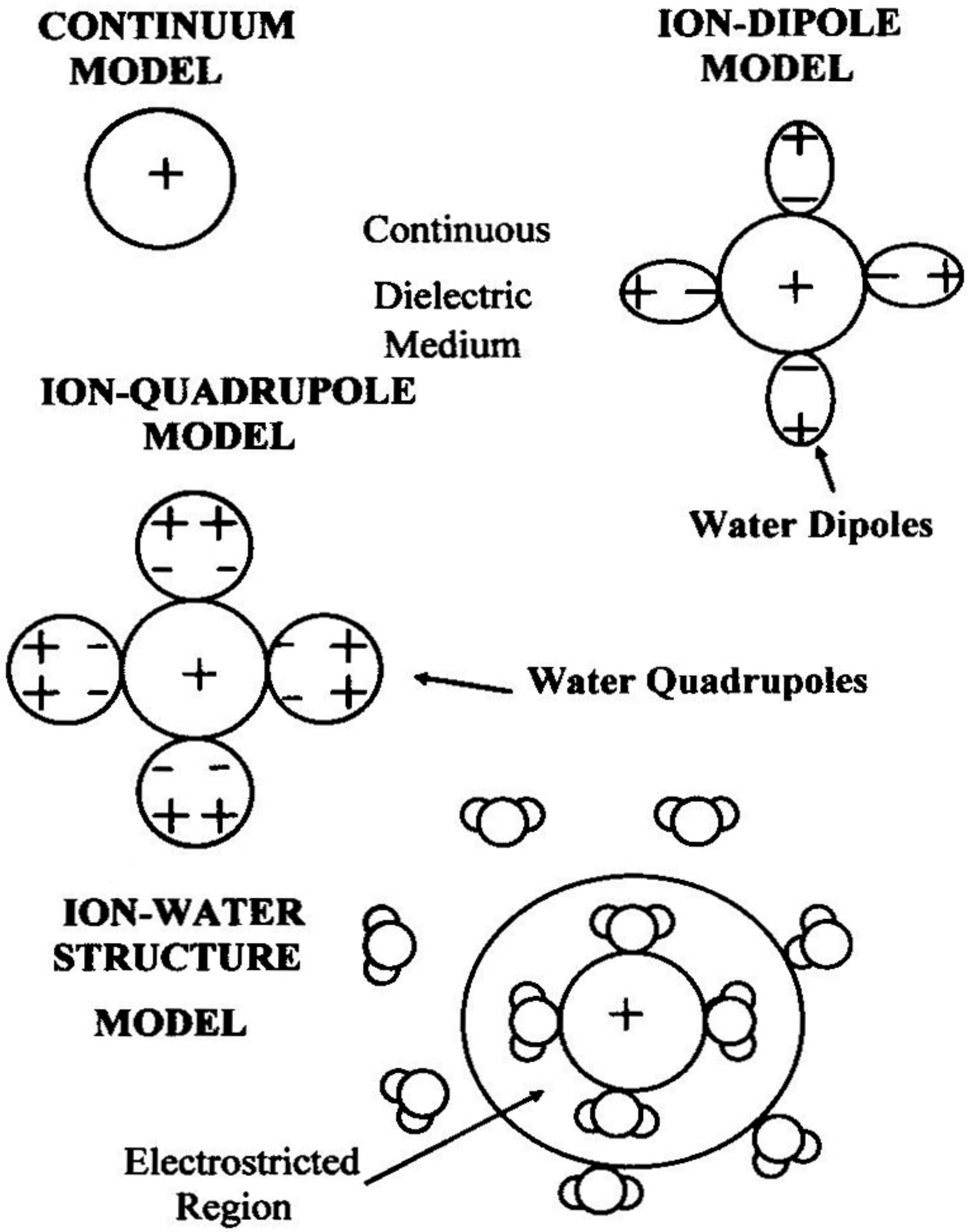
Other Effects Also Occur

Concentration Units

- Salts & other solutes dissolved in water must be specified with respect to their concentration
- Oceanographers generally agree on proper units
- However you will still see every possible unit under the sun being used
- ppm, ppb, ppt, M, mM, μM, nM, mg/L, μg/L, ng/L, pg/L, nmol/kg

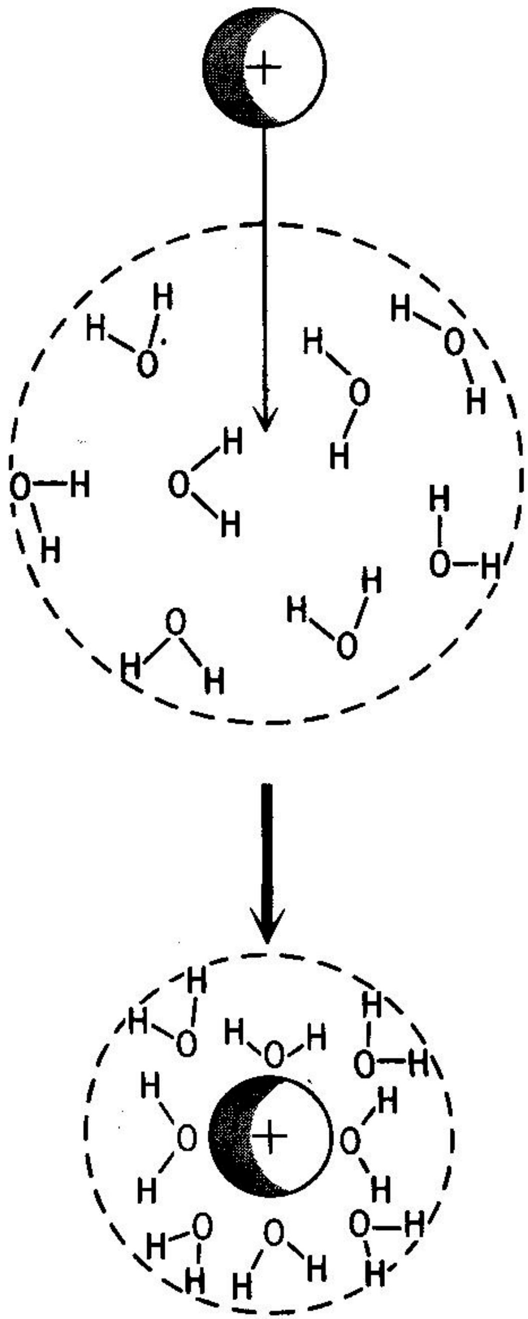
Important Points (see handout)

- Use SI units whenever possible
- Chemical Oceanographers should use mol/kg with a prefix due to compressibility
- You must know whether the unit refers to solvent alone or solution as a whole (i.e., molarity vs. molality; ppm as mg/L or mg/kg)



Discussing Structure Changes in H_2O as Solutes are Added

Millero Fig 4.13 Models to Explain Ion-Water Interactions p 137

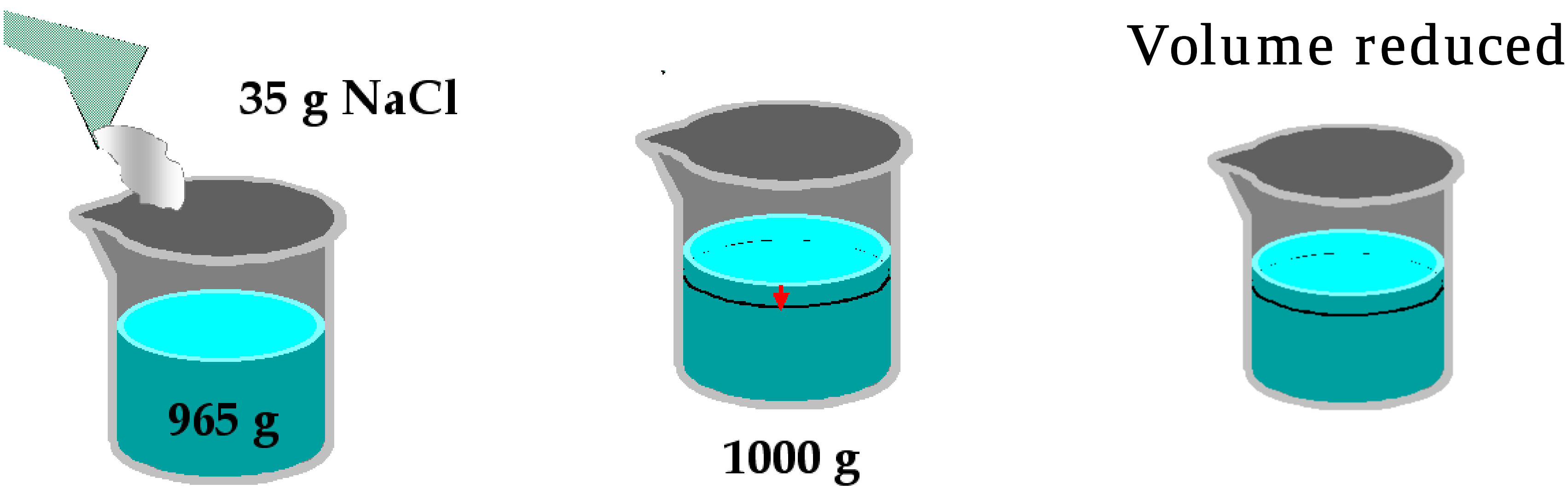


Electrostriction occurs as an ion orients or reorders water molecules causing them to be arranged tightly around the charge center

Libes (1992)

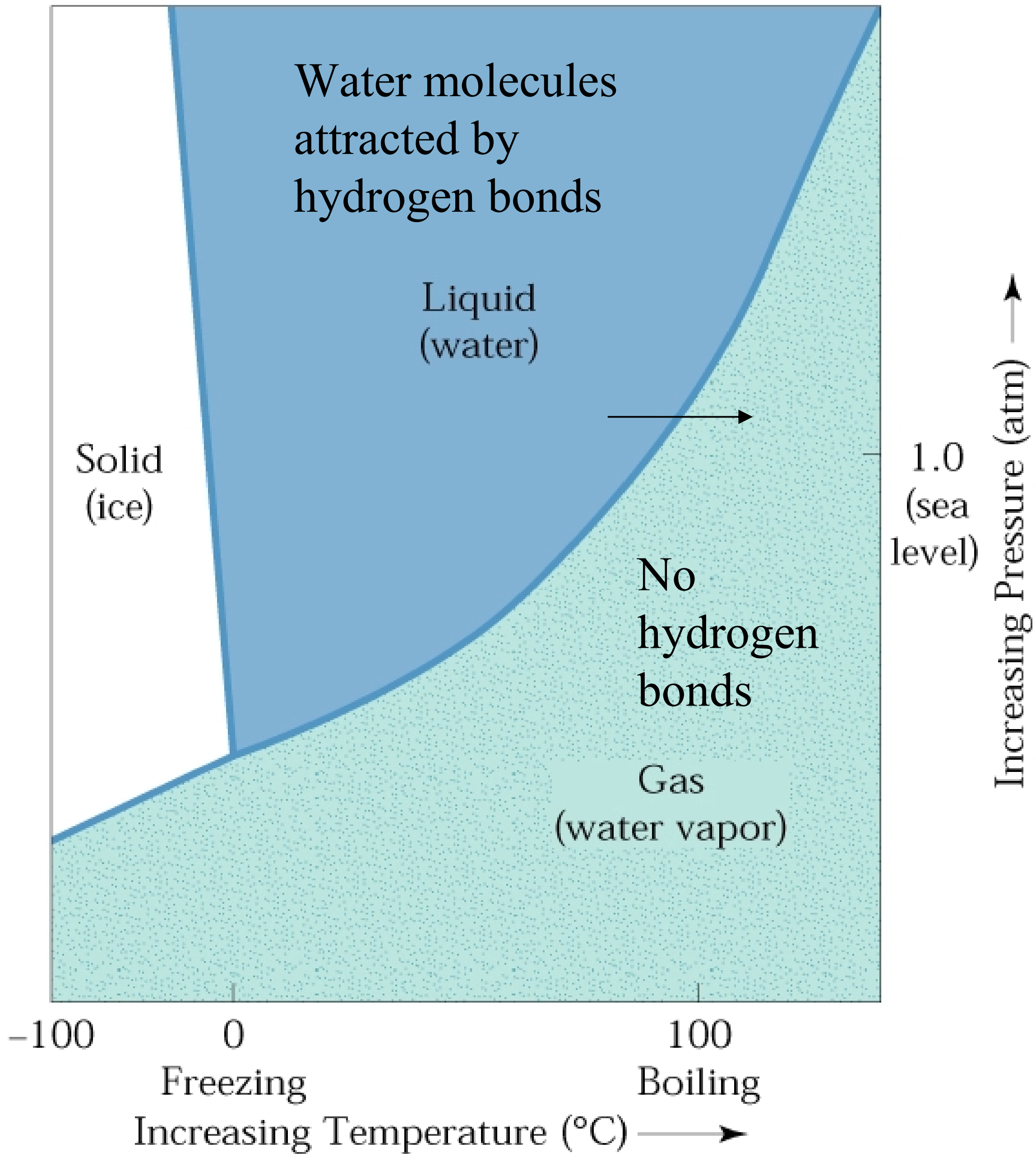
Electrostriction - adding salt to H_2O

- Add 35 g of NaCl to 965 g H_2O = 1000g total
- Density - NaCl 2.165 g/cm^3; H_2O 0.997 g/cm^3
- Volumes = 16.2 cm^3 + 967.9 cm^3 = 984.1 cm^3
- Actual Volume = 977.3 cm^3



Colligative Properties

- Physicochemical Properties that vary with number of species in solution not their chemical nature
- Vapor Pressure Lowering
- Boiling Point Elevation (ΔT_b)
- Freezing Point Depression (ΔT_f)
- Osmotic Pressure (π)



Explanation of Colligative Properties Based on Changes in Phase Equilibria

Simple Phase Diagram of Water

(Wiley 1999)

Vapor Pressure Lowering

Magnitude of vapor pressure (v.p.) lowering can be expressed in terms of solute mole fraction

$\Delta P/P^o = X$ where X = mole fraction (i.e., ratio of moles solute to total moles

P^o = v.p. of pure solvent

ΔP = change in v.p.

Boiling Point Elevation

Boiling point (b.p.) of solution changes

$\Delta T_b = v\, K_b\, m$ where m = molality

K_b = constant for solvent

0.512 $^oC/m$ for H_2O

v = van't Hoff factor

Ions/molecule → ΔT_b = change in b.p.

Freezing Point Depression

Freezing point (m.p.) of solution changes

ΔT_f = - v K_f m where m = molality

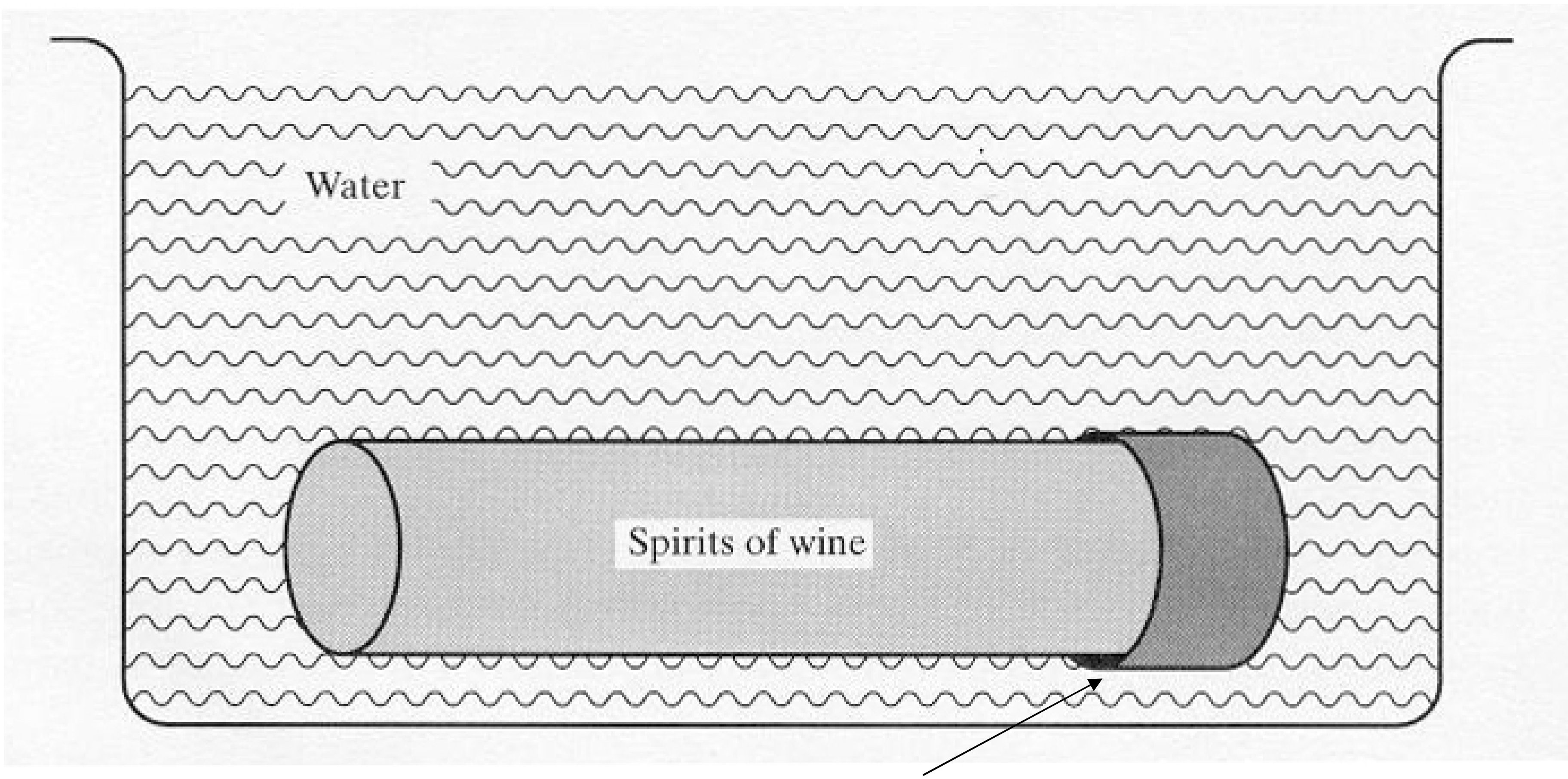
K_f = constant for solvent

1.86 = $^oC/m$ for H_2O

V = van't Hoff factor

Δ T_f = change in m.p.

Osmotic Pressure (π)



Nollet (1748) used pig bladder membrane (Pilson, 1998)

Osmotic Pressure (π)

From the Gas Law ($PV = nRT$)

$$\boldsymbol{\pi V = v\,R\,T}$$

where T = absolute temp.

R = gas constant

v = van't Hoff factor

V = volume

π = osmotic pressure

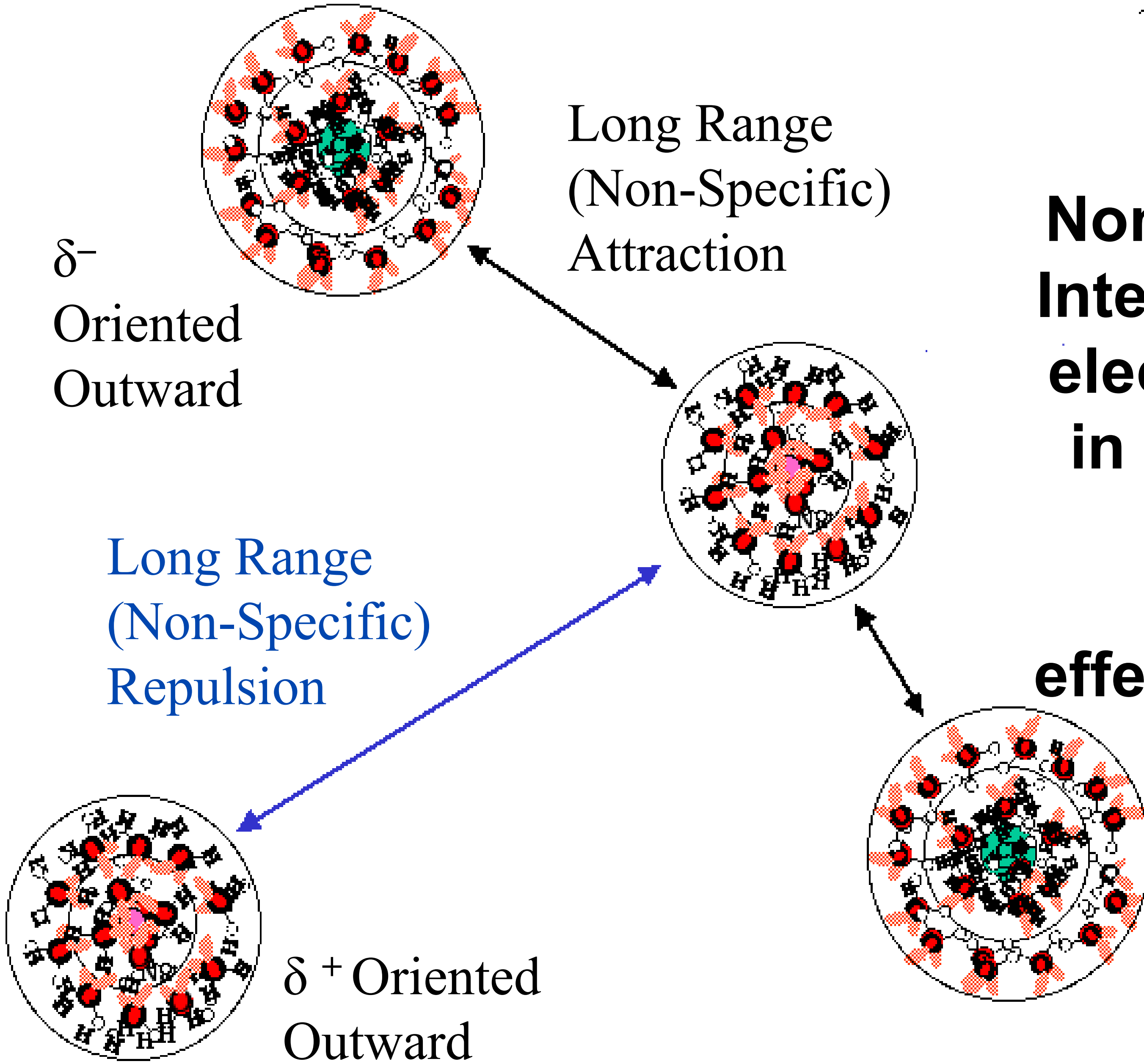
Important Properties

- Electrostriction influences density, water structure & mobility of ions in solution
- It also results in pressure effects for solubility
- Freezing Point Depression lowers freezing point of natural waters especially seawater
- Vapor Pressure Lowering reduces evaporation
- Osmotic Pressure strongly influences diffusion across biological membranes

Ion-Ion Interactions

- Many types – non-specific, bonding, contact, solvent shared, solvent separated
- Non-specific i.e., long range interactions and the concepts of ionic strength, activity & activity coefficient
- Specific interactions e.g. complexation, ion pairing (strong or weak)
- Millero cartoons

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



Non-specific Interactions - electrostatic in nature & limit effectiveness of the ion

Non-specific Interaction

- Electrostatic in nature
- Limits effectiveness of ion in solution
- Use concept of **activity** to quantify effect

(effective concentration)

$\mathbf{a_i = [i]_F \gamma_F(i)}$ where a_i = activity of ion i

$[i]_F$ = free ion conc. (m)

$\gamma_F(i)$ = activity coefficient of ion i

In short $\boxed{\mathbf{a = [i]\,\gamma}}$

Activity of Individual Ion Influenced by Other Ions

- Ionic Strength of solution

$$\mathbf{I = 0.5\ \Sigma\ Z^2\ m}$$

where I = ionic strength
Z = charge on ion
m = molal conc.

$$\boxed{\mathbf{a = [i]\ \gamma}}$$