

Chemical Oceanography 2022



Dr. David K. Ryan

Department of Chemistry

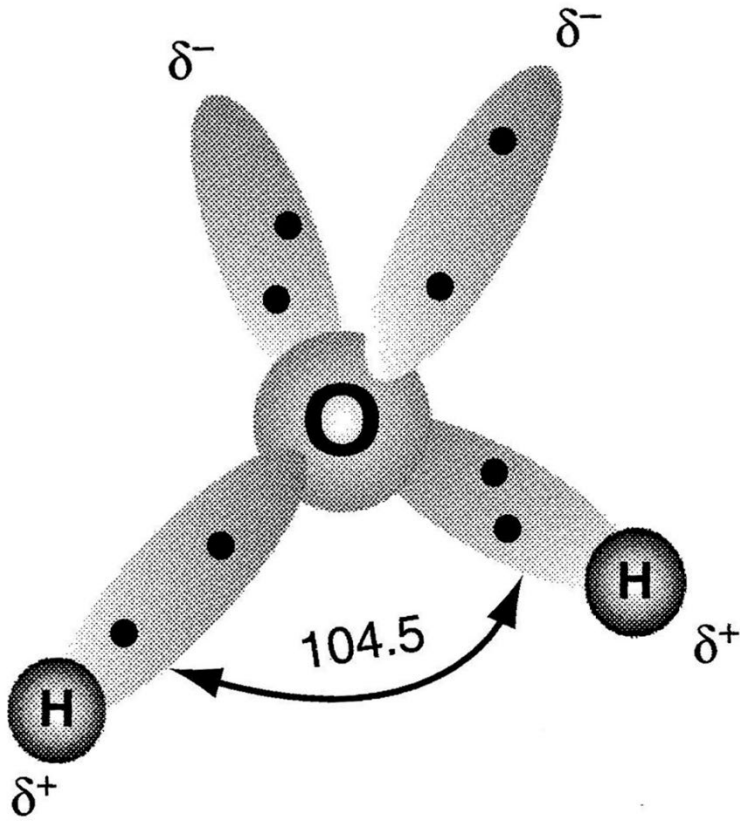
University of Massachusetts Lowell

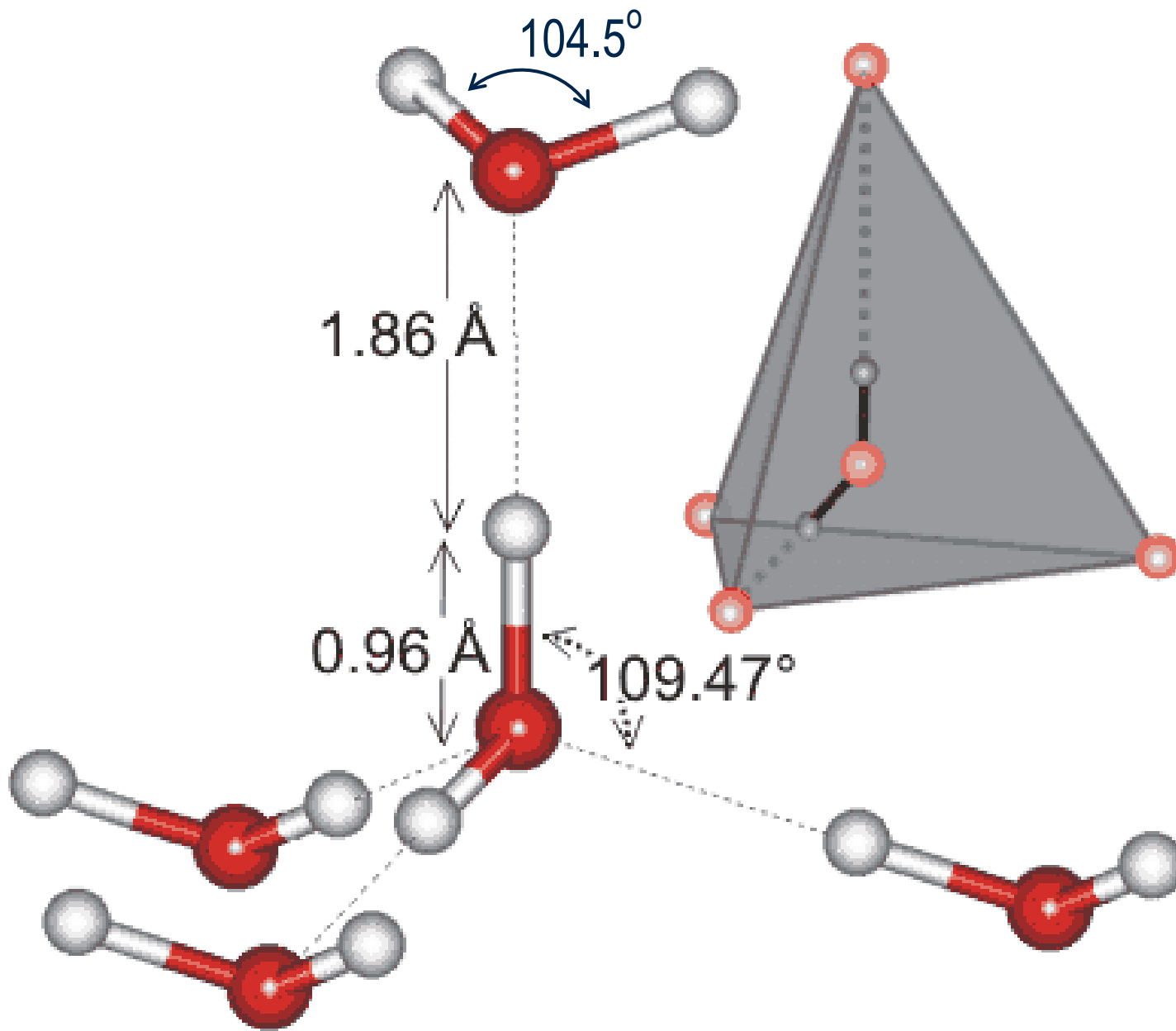
&

Intercampus of Marine Sciences Program

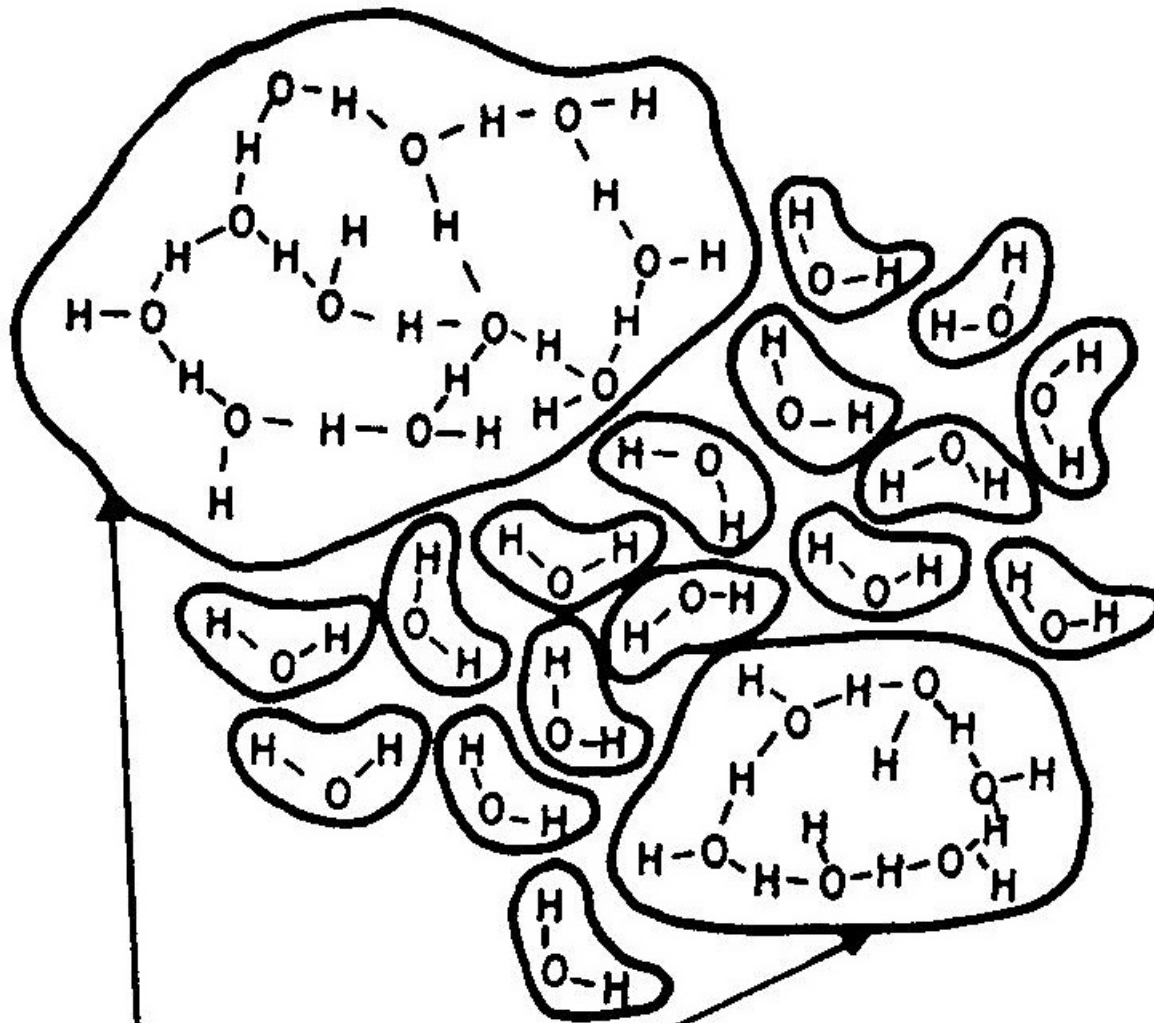
http://faculty.uml.edu/David_Ryan/84.653

Water Quadrupole





Arrangement for Hydrogen Bonding - Pentamer

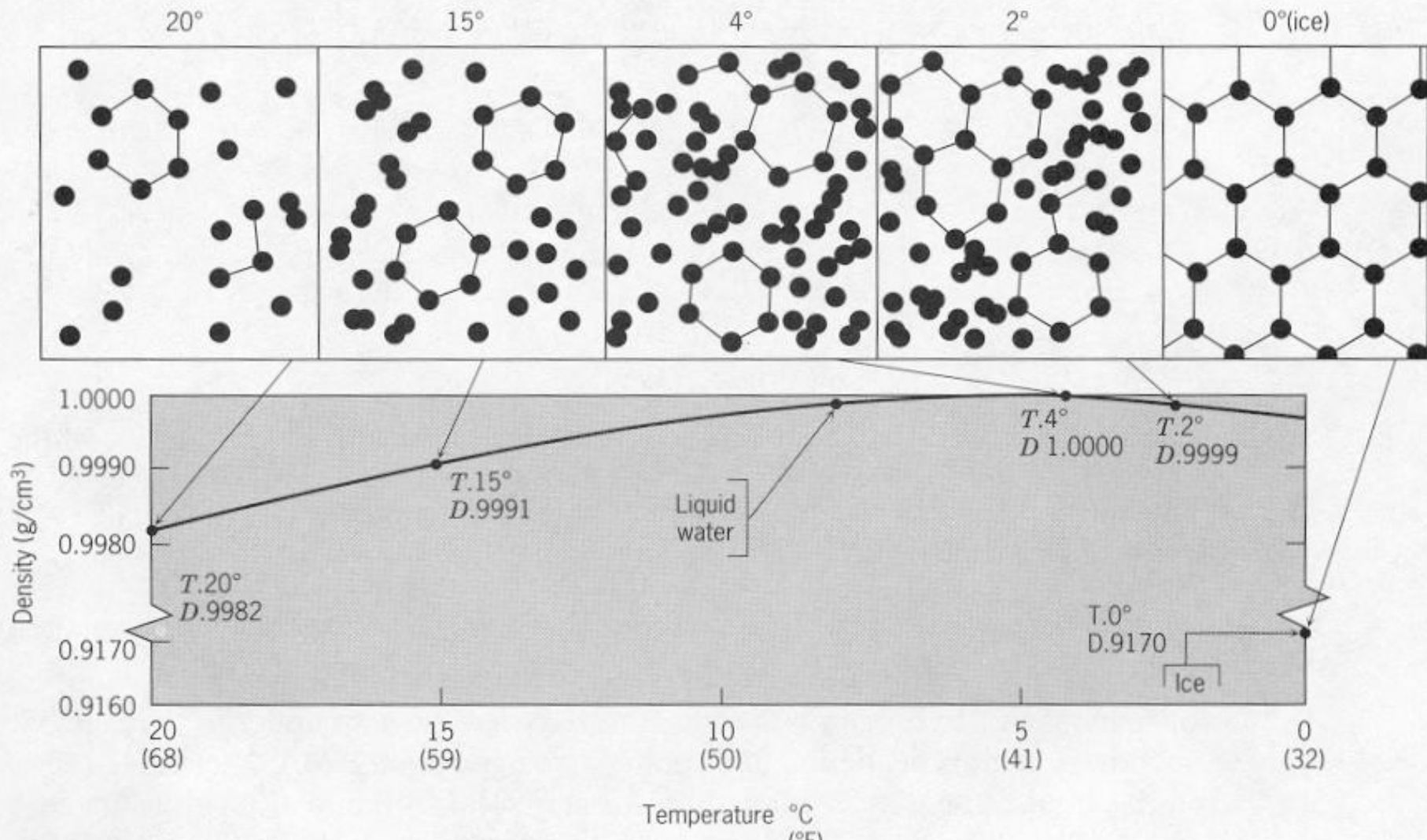


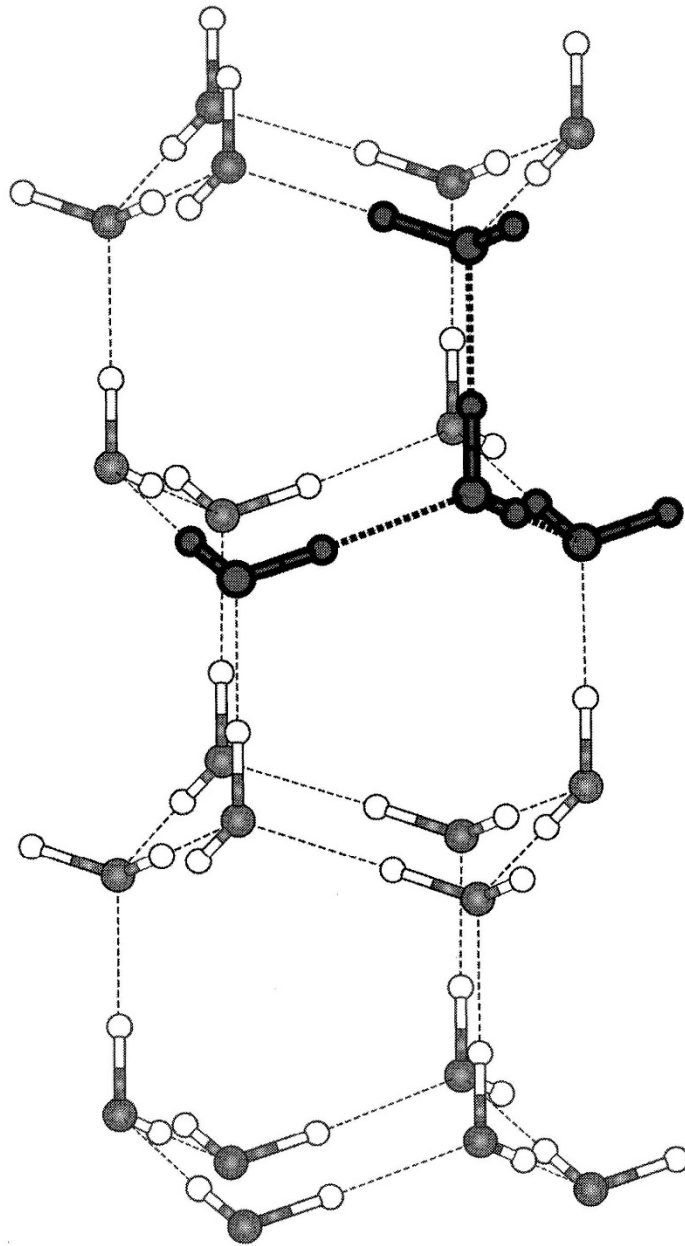
**Water
Clusters
Dynamically
Form, Break
and Re-form**

(Millero 2006)

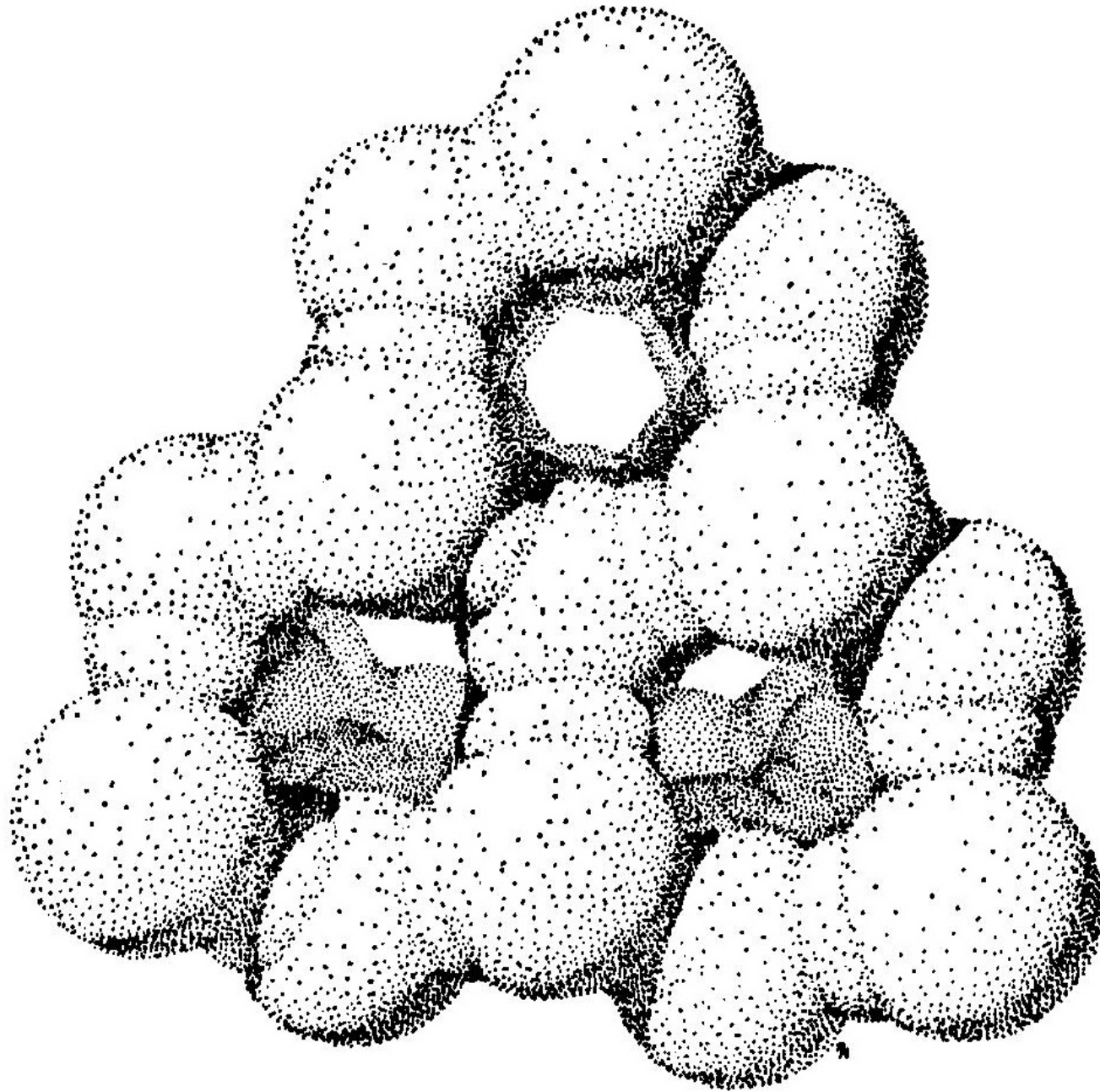
Clusters

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





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

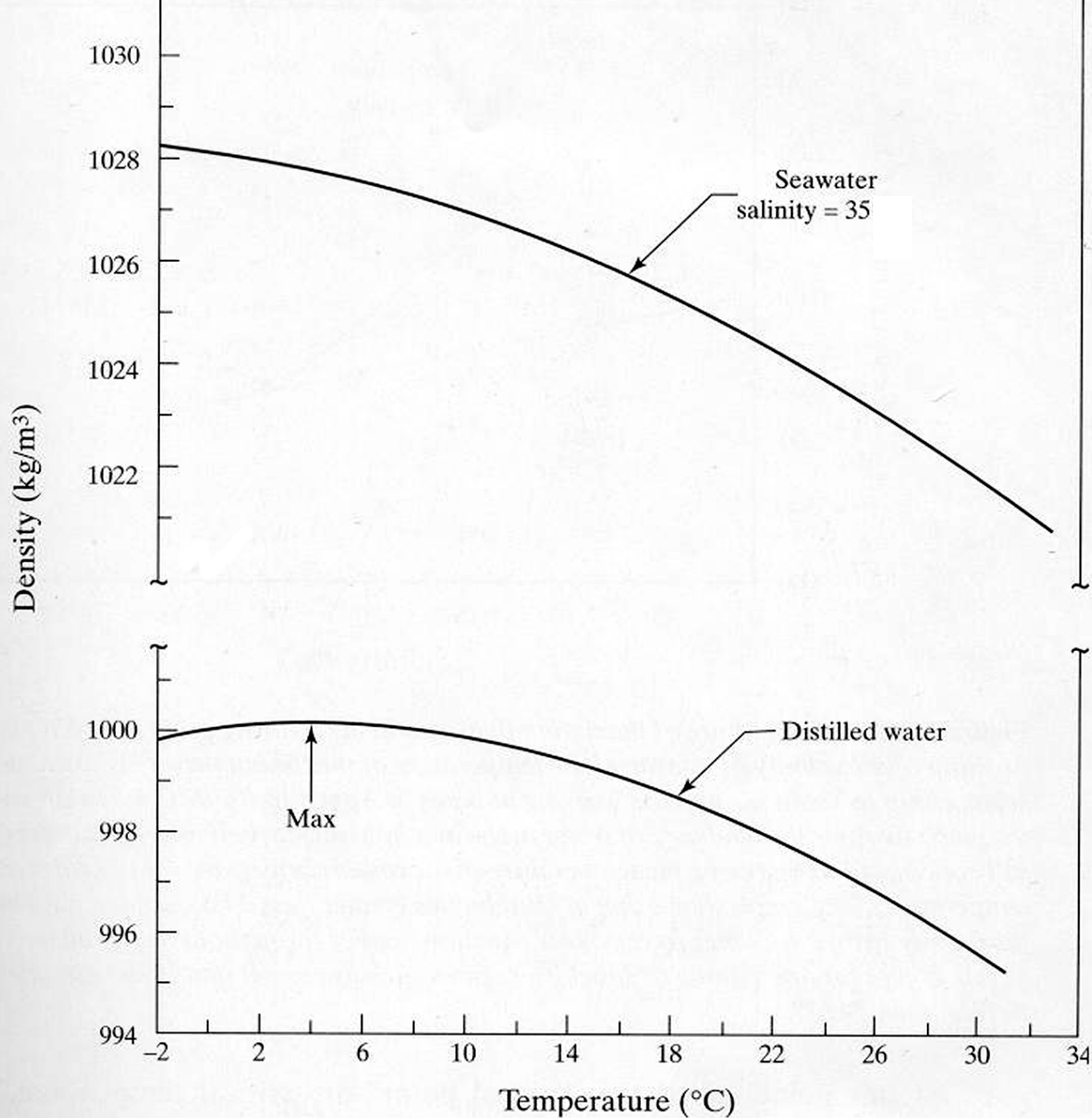


**Structure
of Ice 1h,
Hexagonal
with Space
Giving Low
Density**

(Pilson 1998)

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)

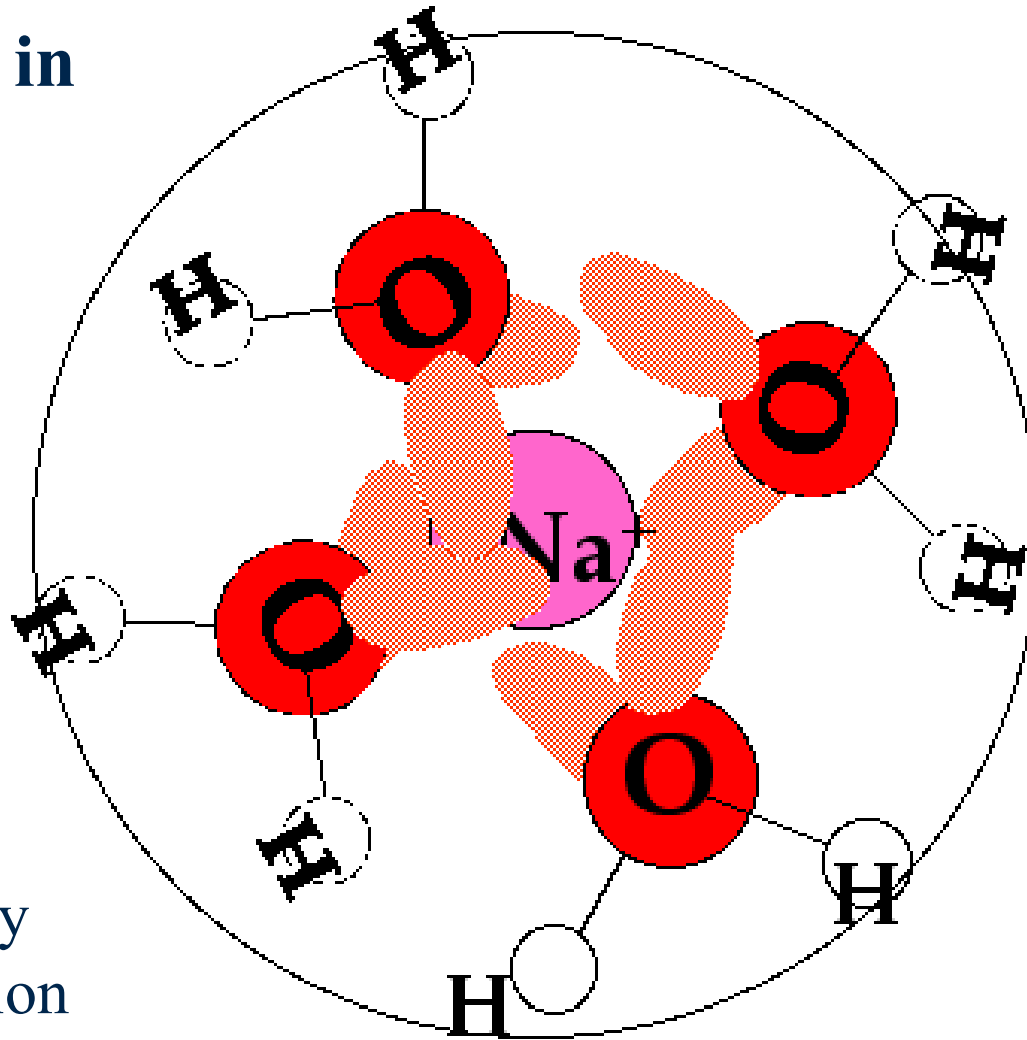
TABLE 2.2**Comparison of Pure Water and Seawater Properties**

<i>Property</i>	<i>Seawater, 35‰ S</i>	<i>Pure Water</i>
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

**Some
Properties
Undergo
Dramatic
Changes**

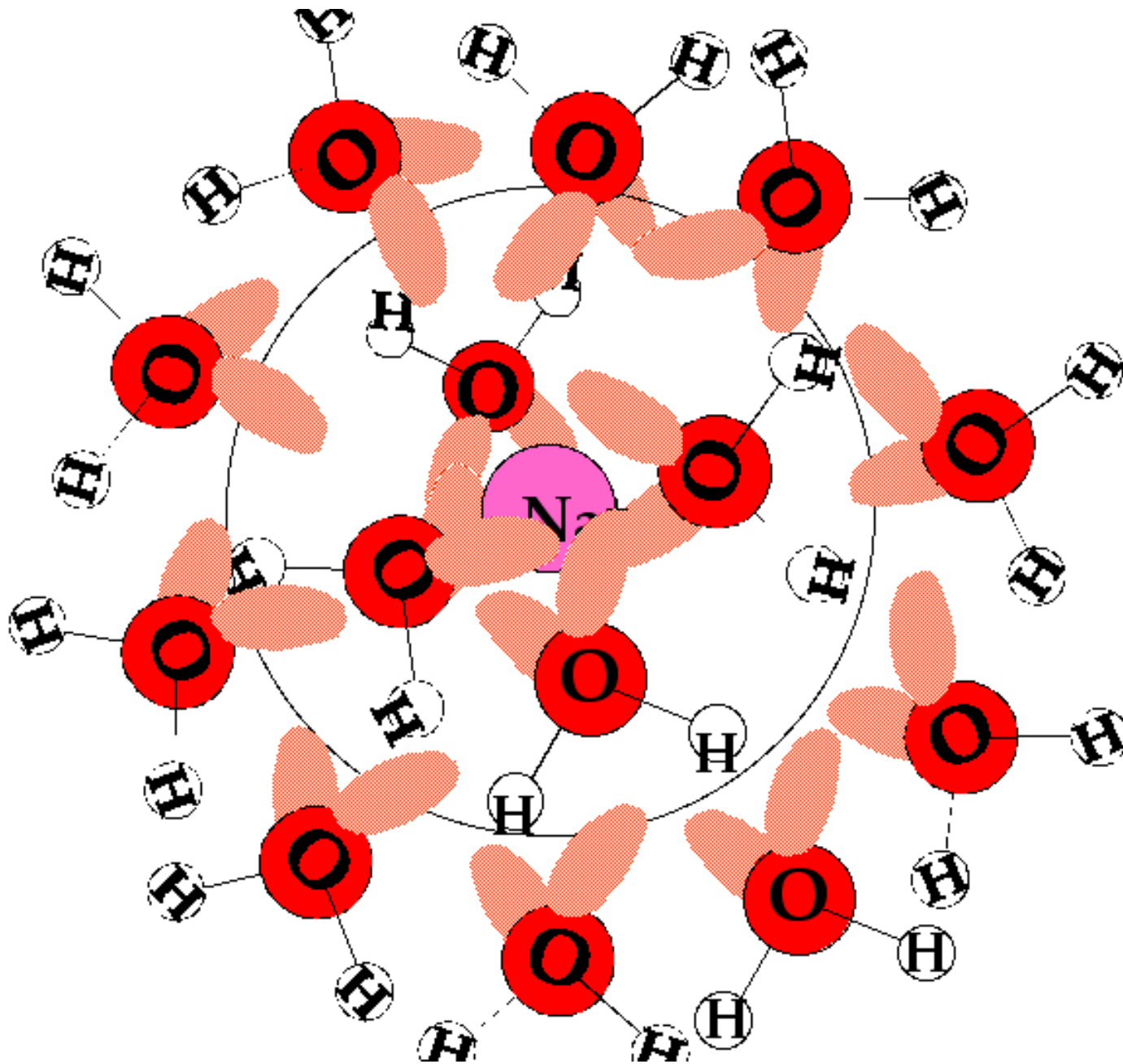
Source: From *Marine Chemistry*, R. A. Horne, copyright © 1969 by John Wiley & Sons, Inc., New York, p. 57. Reprinted with permission.

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



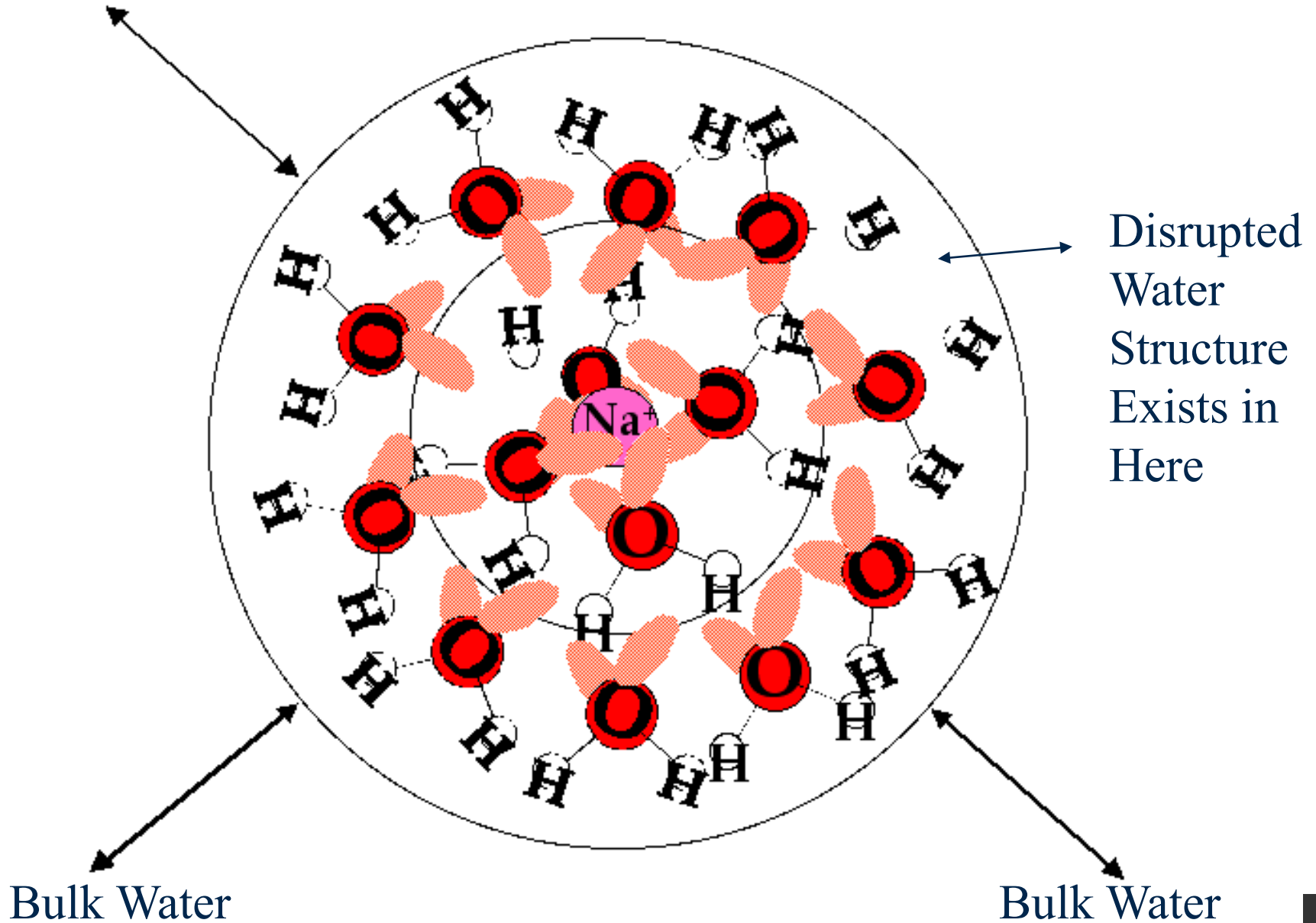
Primary
Solvation
Shell of H_2O

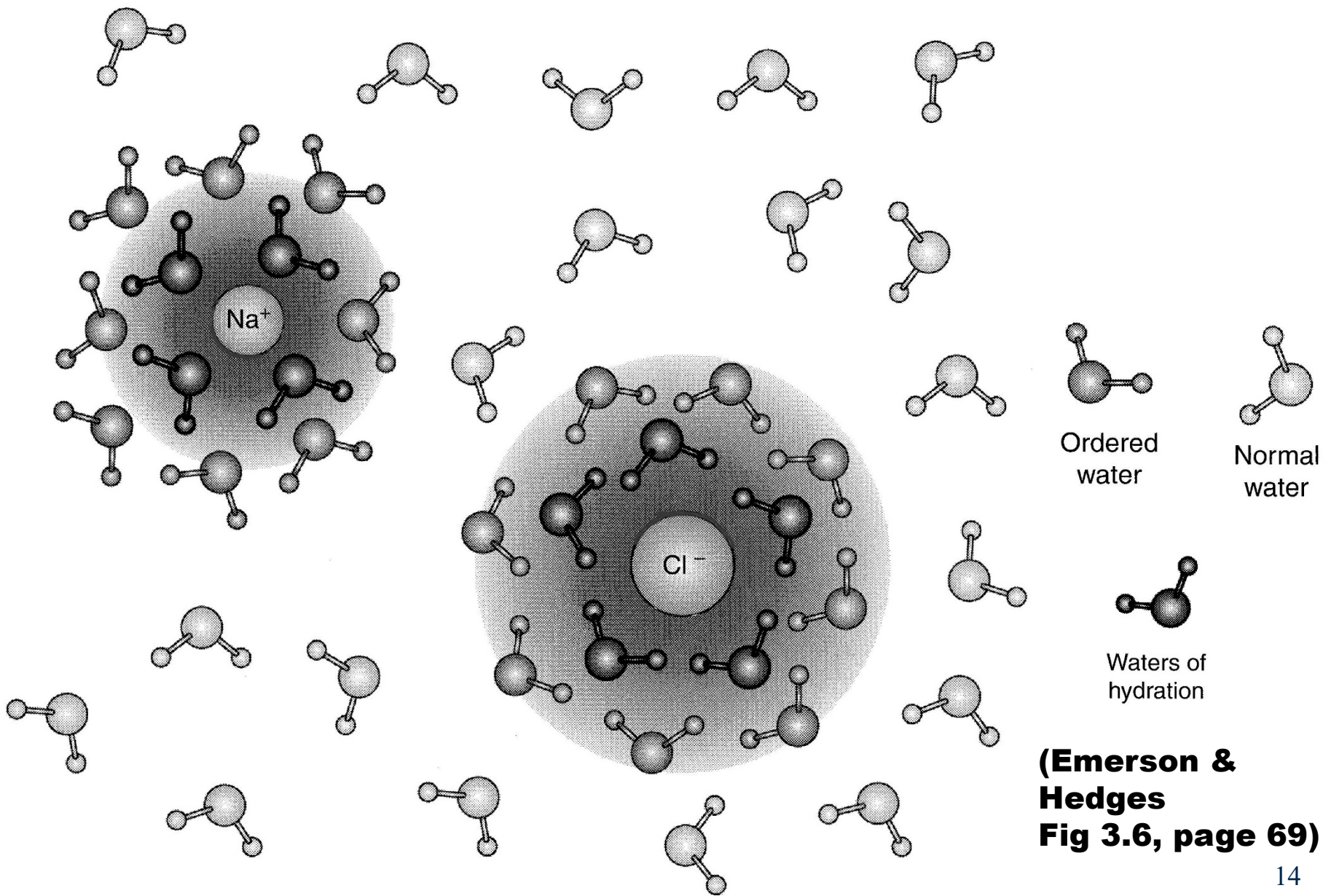
Polarity, High
Dielectric
Constant
Result in
Strong
Solvation or
Hydration of
 Na^+ by H_2O



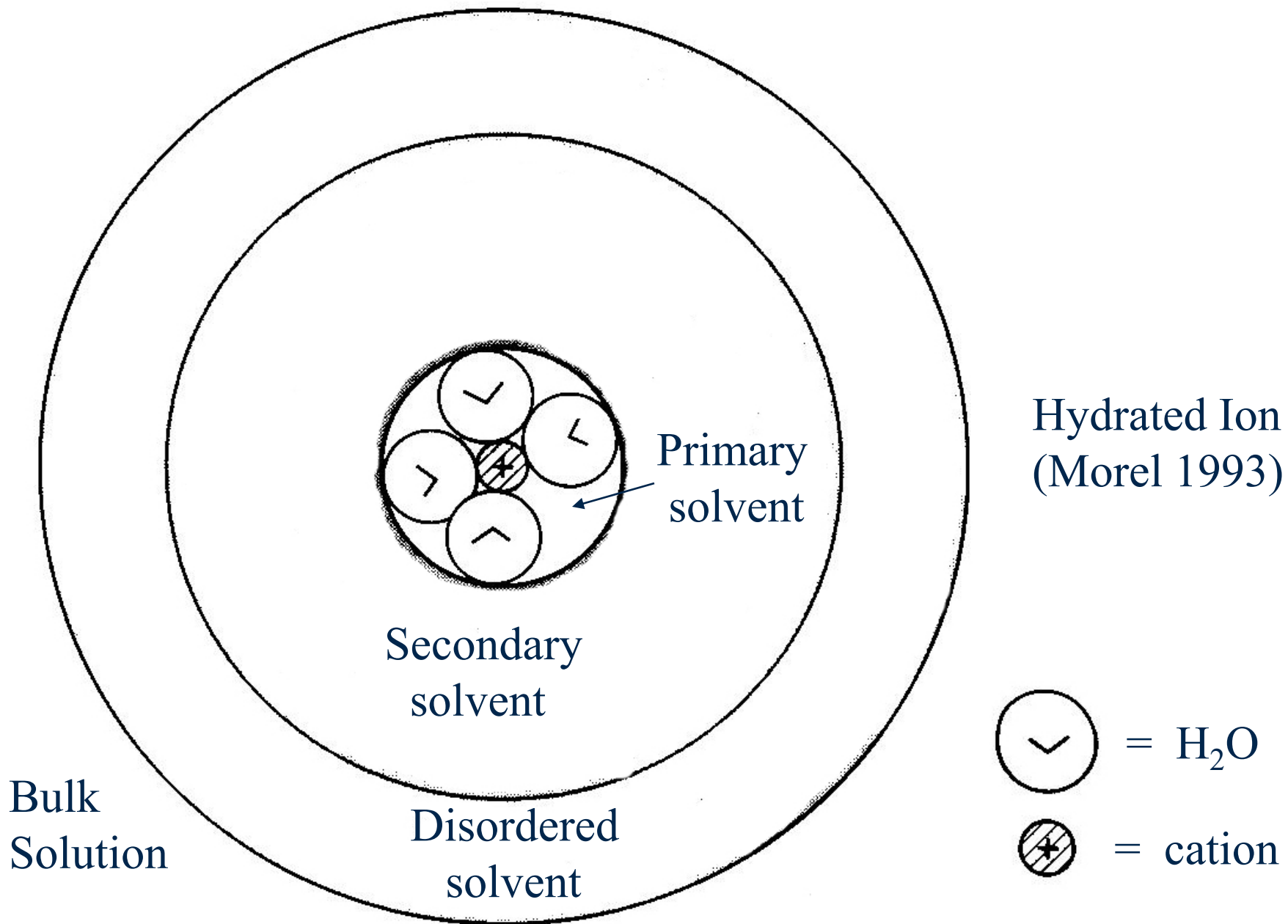
Secondary
Solvation
Shell or a
Second
Sphere of
 H_2O is
Bound to
the First

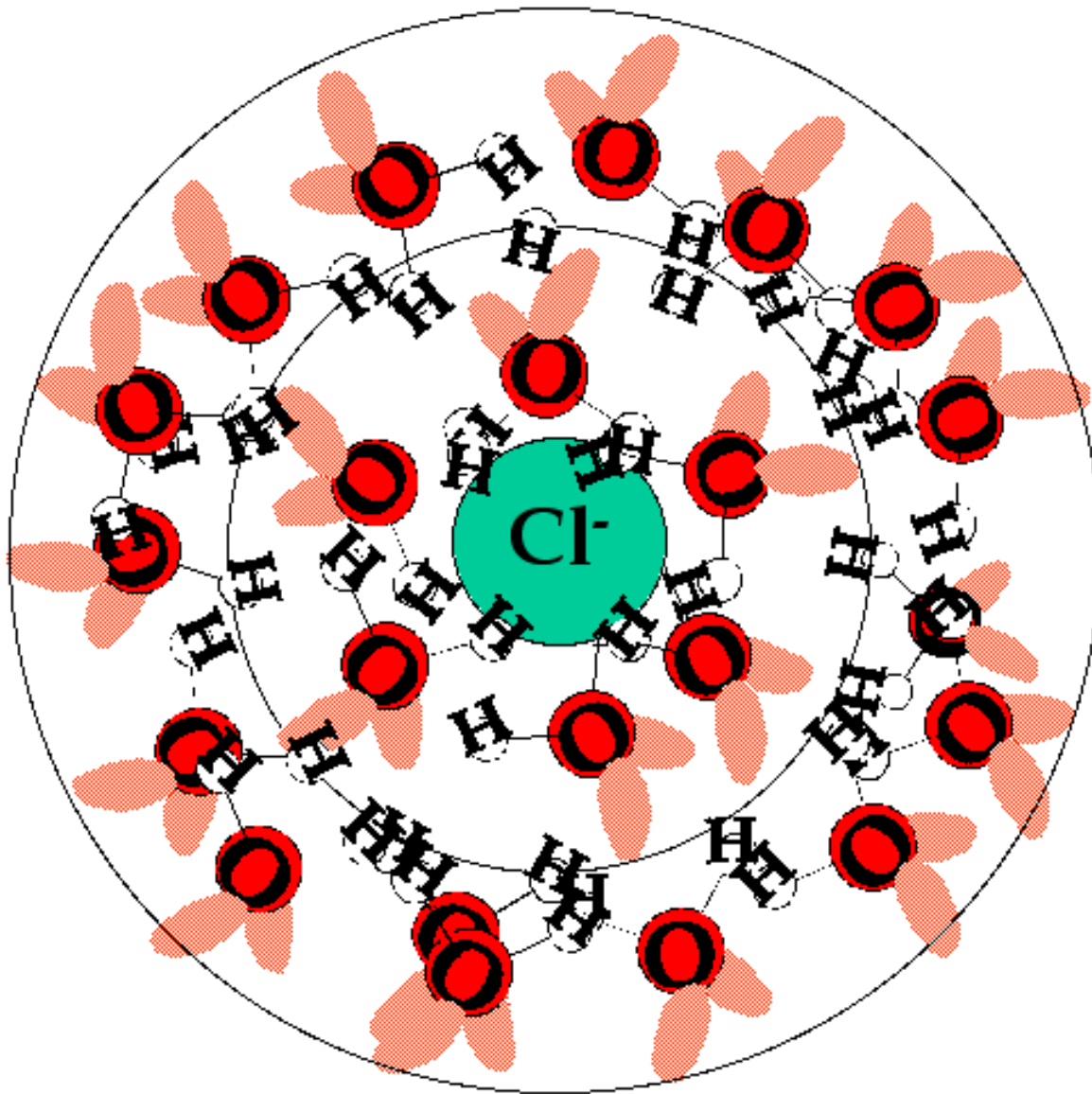
Normal H₂O Structure Exists Out Here for “Bulk” Water



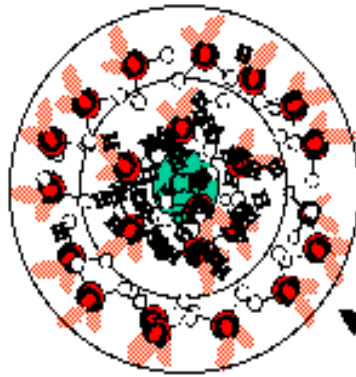


**(Emerson &
Hedges
Fig 3.6, page 69)**



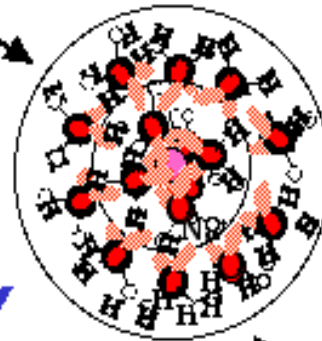


For Anions the
Concept is
Analogous
Only Reversed
With Respect to
the Orientation
of the H_2O

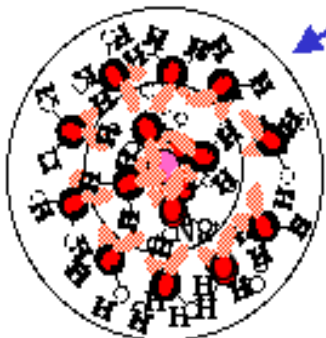


Long Range
(Non-Specific)
Attraction

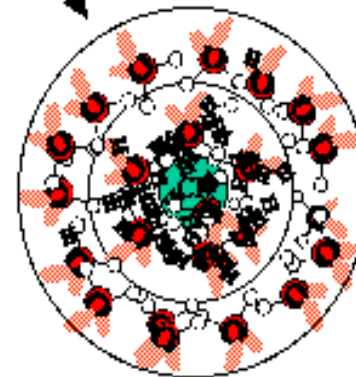
δ^-
Oriented
Outward



Long Range
(Non-Specific)
Repulsion



δ^+ Oriented
Outward



Other
Effects
Also
Occur

Concentration Units

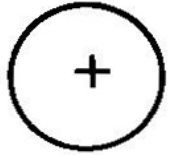
- # Salts & other solutes dissolved in water must be specified with respect to their concentration
- # Oceanographers generally agree on proper units
- # However you will still see every possible unit under the sun being used
- # ppm, ppb, ppt, M, mM, μ M, nM, mg/L, μ g/L, ng/L, pg/L, nmol/kg

Important Points

(see handout posted for last class)

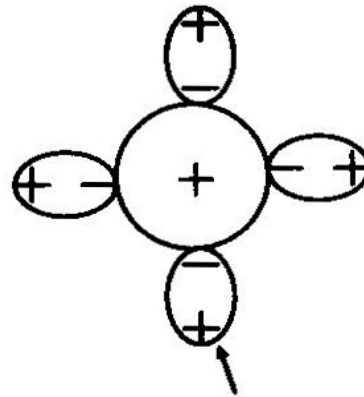
- # Use SI units whenever possible
- # Chemical Oceanographers should use mol/kg with a prefix due to compressibility
- # You must know whether the unit refers to solvent alone or solution as a whole (i.e., molarity vs. molality; ppm as mg/L or mg/kg)

CONTINUUM MODEL



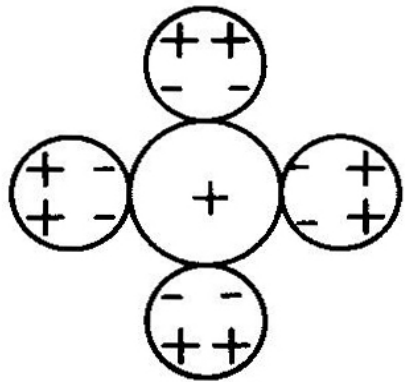
Continuous
Dielectric
Medium

ION-DIPOLE MODEL



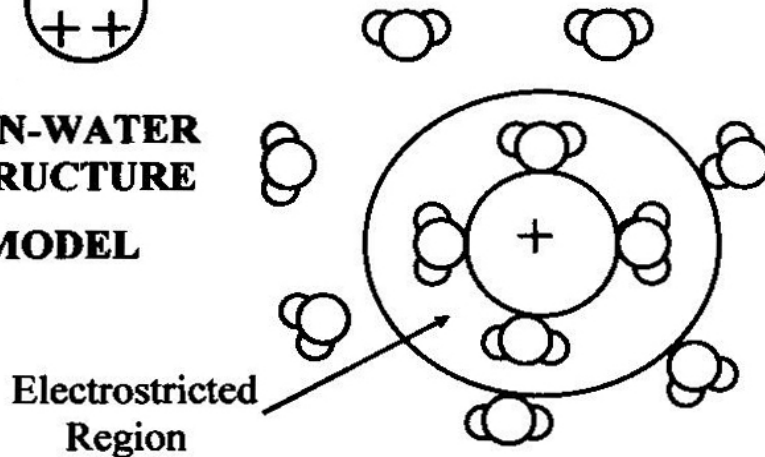
Water Dipoles

ION-QUADRUPOLE MODEL



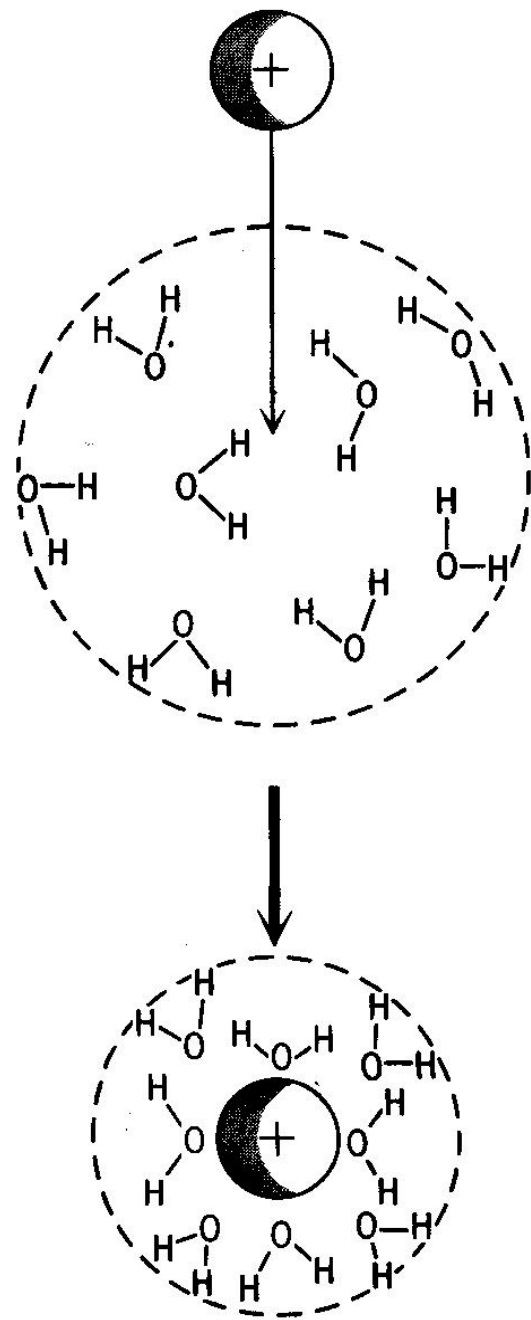
Water Quadrupoles

ION-WATER STRUCTURE MODEL



Discussing
Structure
Changes in H₂O
as Solutes are
Added

Millero Fig 4.13
Models to Explain
Ion-Water
Interactions p 135



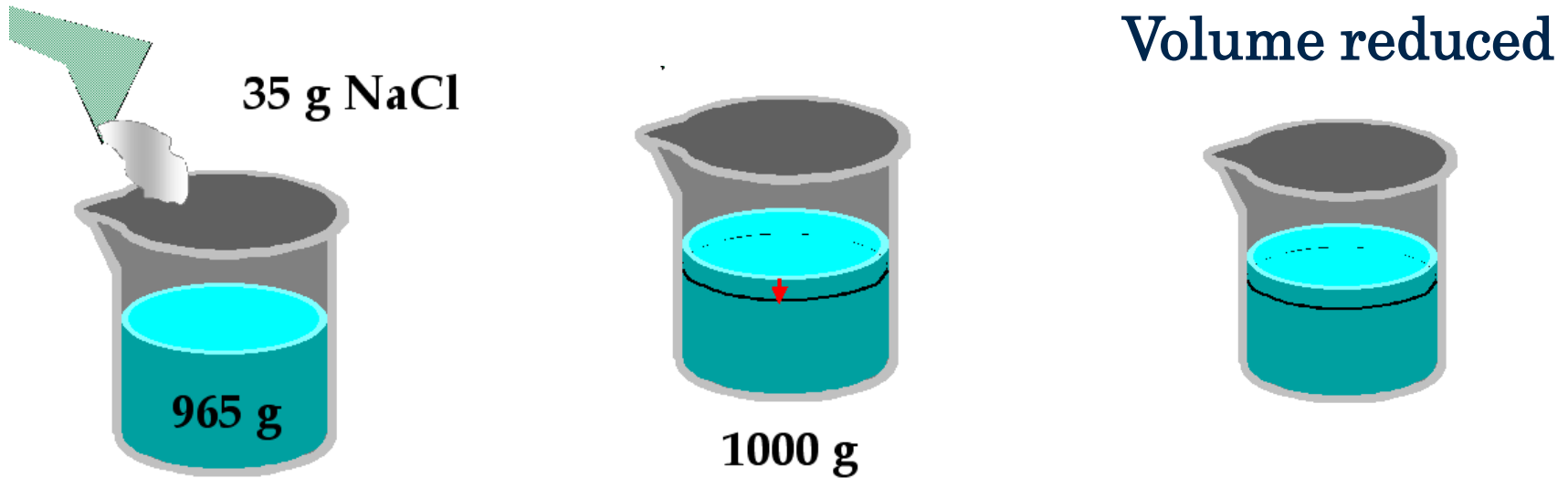
Electrostriction occurs as an ion orients or reorders water molecules causing them to be arranged tightly around the charge center

Libes (1992)

Electrostriction

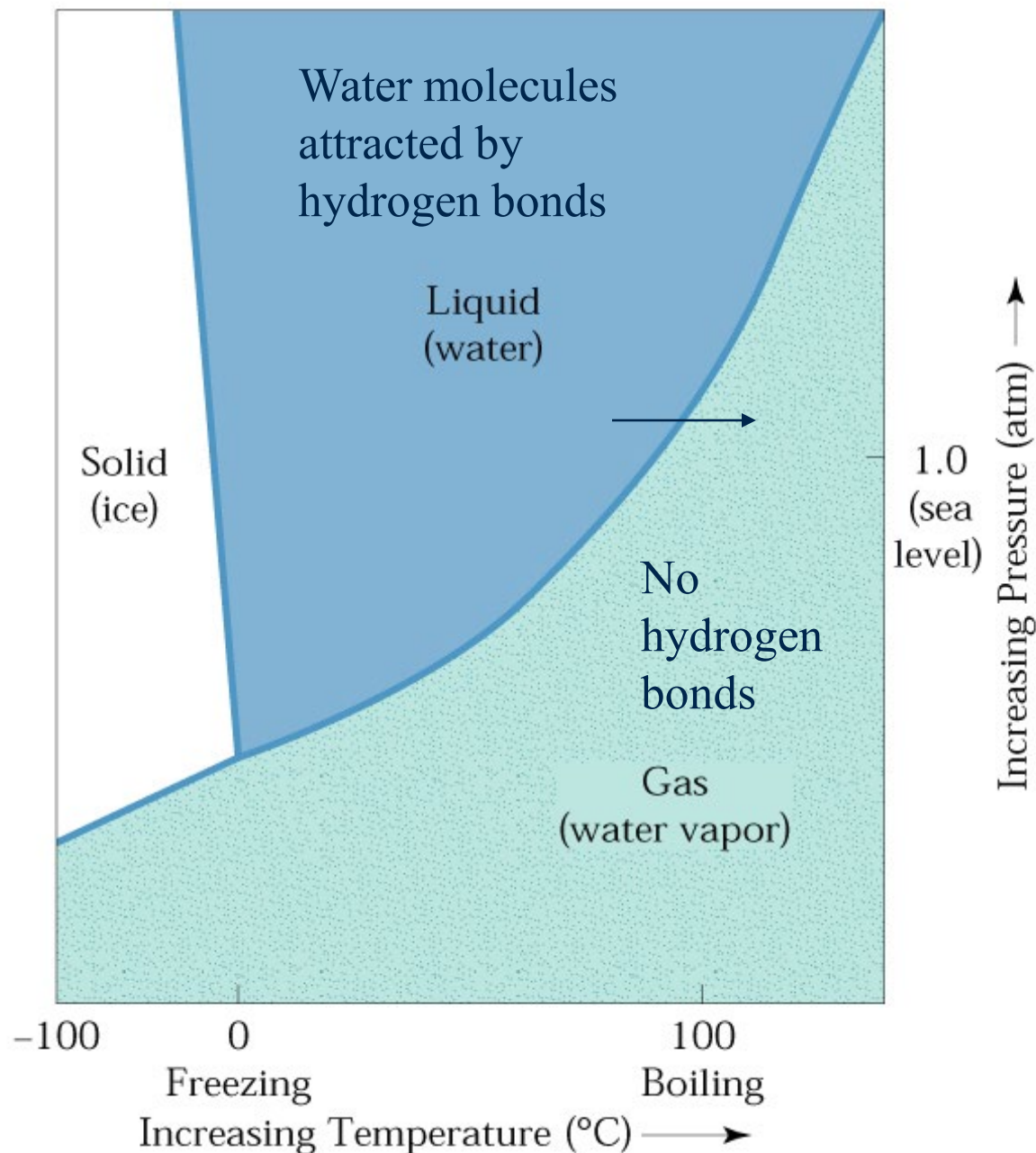
- occurs when adding salt to H₂O

- # Add 35 g of NaCl to 965 g H₂O = 1000g total
- # Density - NaCl 2.165 g/cm³; H₂O 0.9997 g/cm³
- # Volumes = 16.2 cm³ + 967.9 cm³ = 984.1 cm³
- # Actual Volume = 977.3 cm³



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

$\Delta P/P^0 = X$ where X = mole fraction (i.e.,
ratio of moles
solute to total moles

P^0 = v.p. of pure solvent

ΔP = change in v.p.

Boiling Point Elevation

Boiling point (b.p.) of solution changes

$$\Delta T_b = v K_b m \quad \text{where } m = \text{molality}$$

K_b = constant for solvent

0.512 °C/m for H₂O

Ions/molecule \longrightarrow v = van't Hoff factor

ΔT_b = change in b.p.

Freezing Point Depression

Freezing point (m.p.) of solution changes

$$\Delta T_f = - \nu K_f m \quad \text{where } m = \text{molality}$$

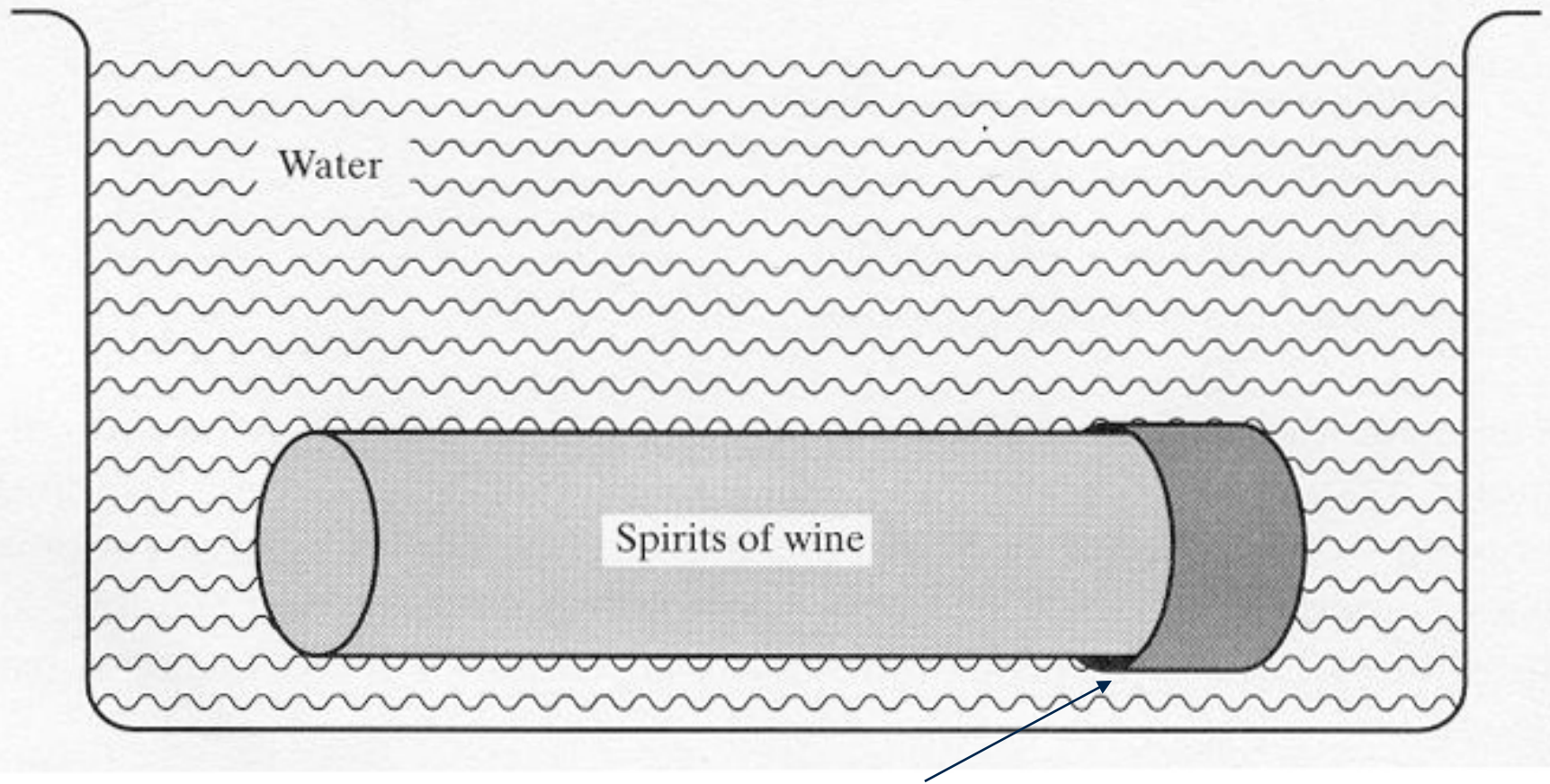
K_f = constant for solvent

1.86 = °C/m for H₂O

ν = van't Hoff factor

ΔT_f = change in m.p.

Osmotic Pressure (π)



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

Osmotic Pressure (π)

From the Gas Law ($PV = nRT$)

$$\pi V = v R T$$

where T = absolute temp.

R = gas constant

v = van't Hoff factor

V = volume

π = osmotic pressure

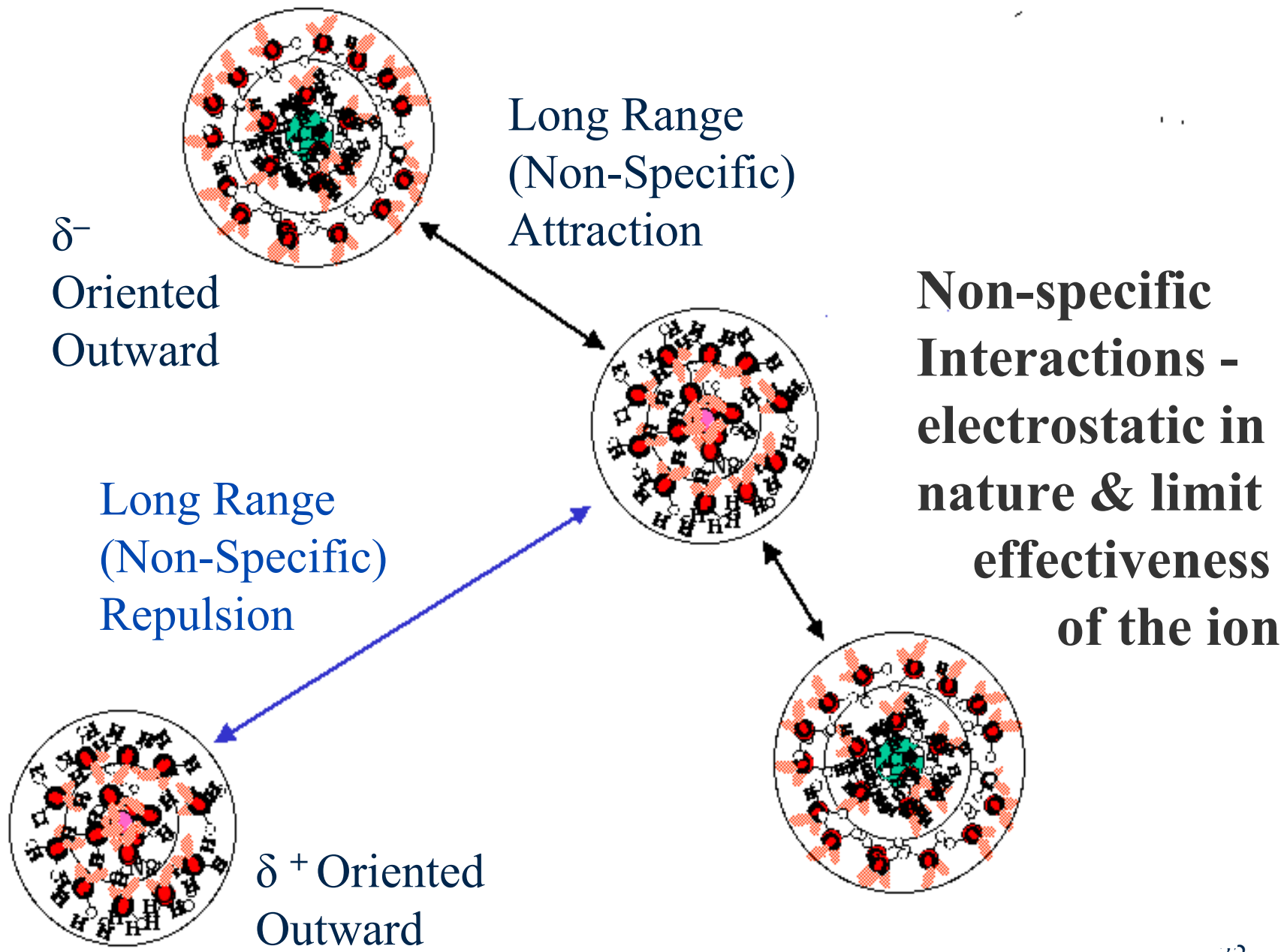
Important Properties

- # 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 Interaction

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

(activity = effective concentration, accounts for non-ideal behavior)

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

$[\mathbf{i}]_F = \text{free ion conc. (m)}$
 $\gamma_F(\mathbf{i}) = \text{activity coefficient}$

In short $\mathbf{a} = [\mathbf{i}] \gamma$ of ion i

Activity of Individual Ion Influenced by Other Ions

Ionic Strength of solution

$$I = 0.5 \sum Z^2 m$$

where I = ionic strength

Z = charge on ion

m = molal conc.

(molarity or molinity

can also be used)

$$a = [i] \gamma$$

Activity Coefficient (γ)

Debye-Huckel Theory is starting point

(Primarily for very low ionic strength)

$$\ln \gamma_{\pm} = - A Z^2 I^{0.5} \quad \text{original D.H.}$$

or

$$\ln \gamma_{\pm} = - S_f I^{0.5} / (1 + A_f a I^{0.5}) \quad \text{extended}$$

Where γ_{\pm} is the mean ion activity coefficient

S_f , A & A_f are constants related to temperature

I is ionic strength & a is the ion size parameter in \AA

Z is the charge on the ion

Activity Coefficient (γ)

Guntelberg Approximation

$$\ln \gamma_{\pm} = - A Z^2 [I^{0.5}/(1 + I^{0.5})]$$

Where γ_{\pm} is the mean ion activity coefficient

A is a constant

I is ionic strength

Z is the charge on the ion

Useful for
 $I \geq 0.1$

Activity Coefficient (γ)

Davies Equation

$$\ln \gamma_{\pm} = - A Z^2 [I^{0.5}/(1 + I^{0.5}) - 0.2 I]$$

Where γ_{\pm} is the mean ion activity coefficient

A is a constant (= 1.17)

I is ionic strength

Z is the charge on the ion

Useful for
I ~ 0.5

Activity Coefficient (γ)

Bronsted-Guggenheim

$$\ln \gamma_{\pm} = \ln \gamma_{\text{DH}} + \sum_j B_{ij}[j] + \sum_j \sum_k C_{ijk}[j][k] + \dots$$

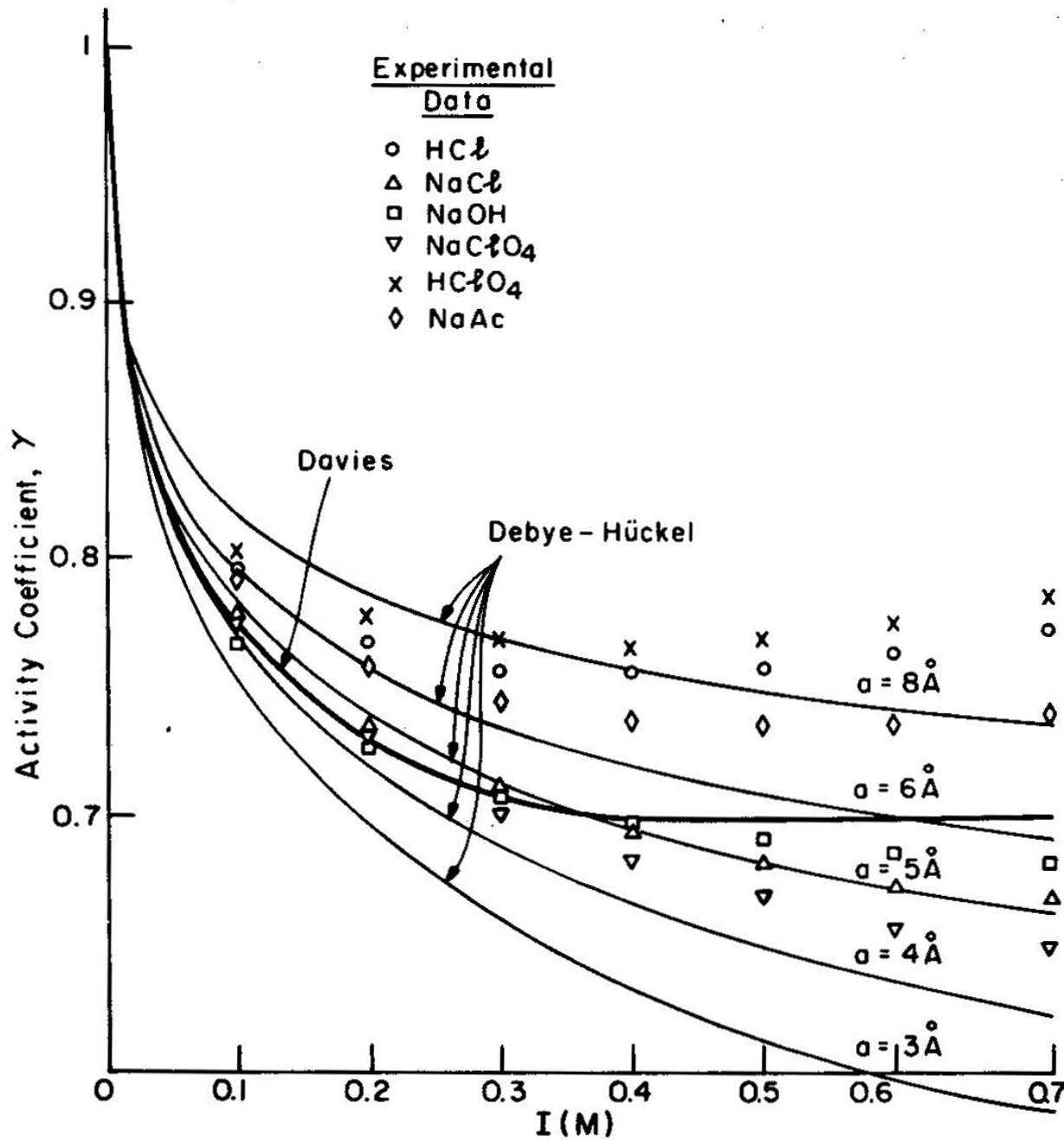
Where γ_{\pm} is the mean ion activity coefficient

γ_{DH} is the γ from Debye-Huckel

B_{ij} is a virial coefficient for ion pairs

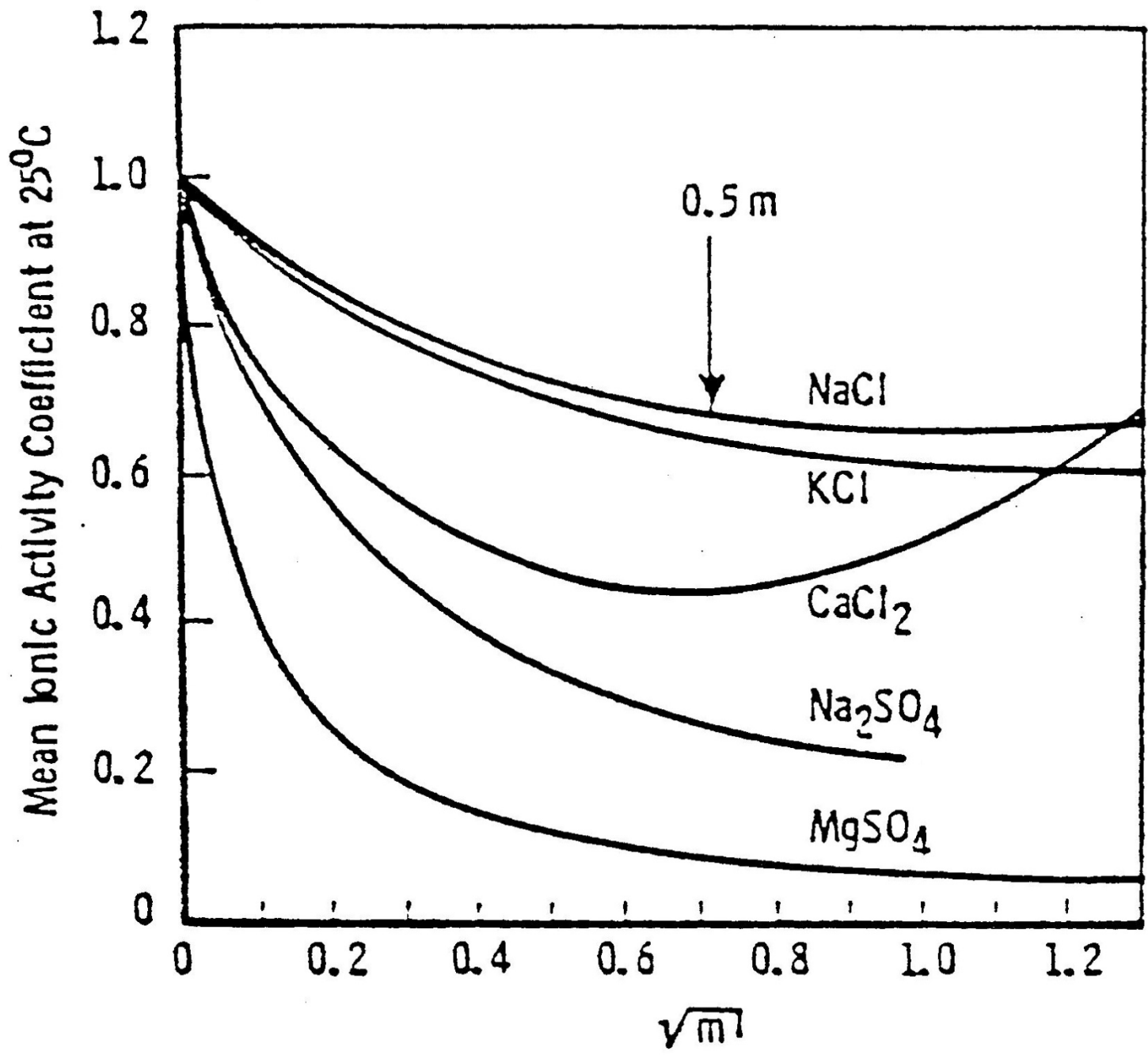
C_{ijk} is a virial coefficient for three ions

Useful at
any I

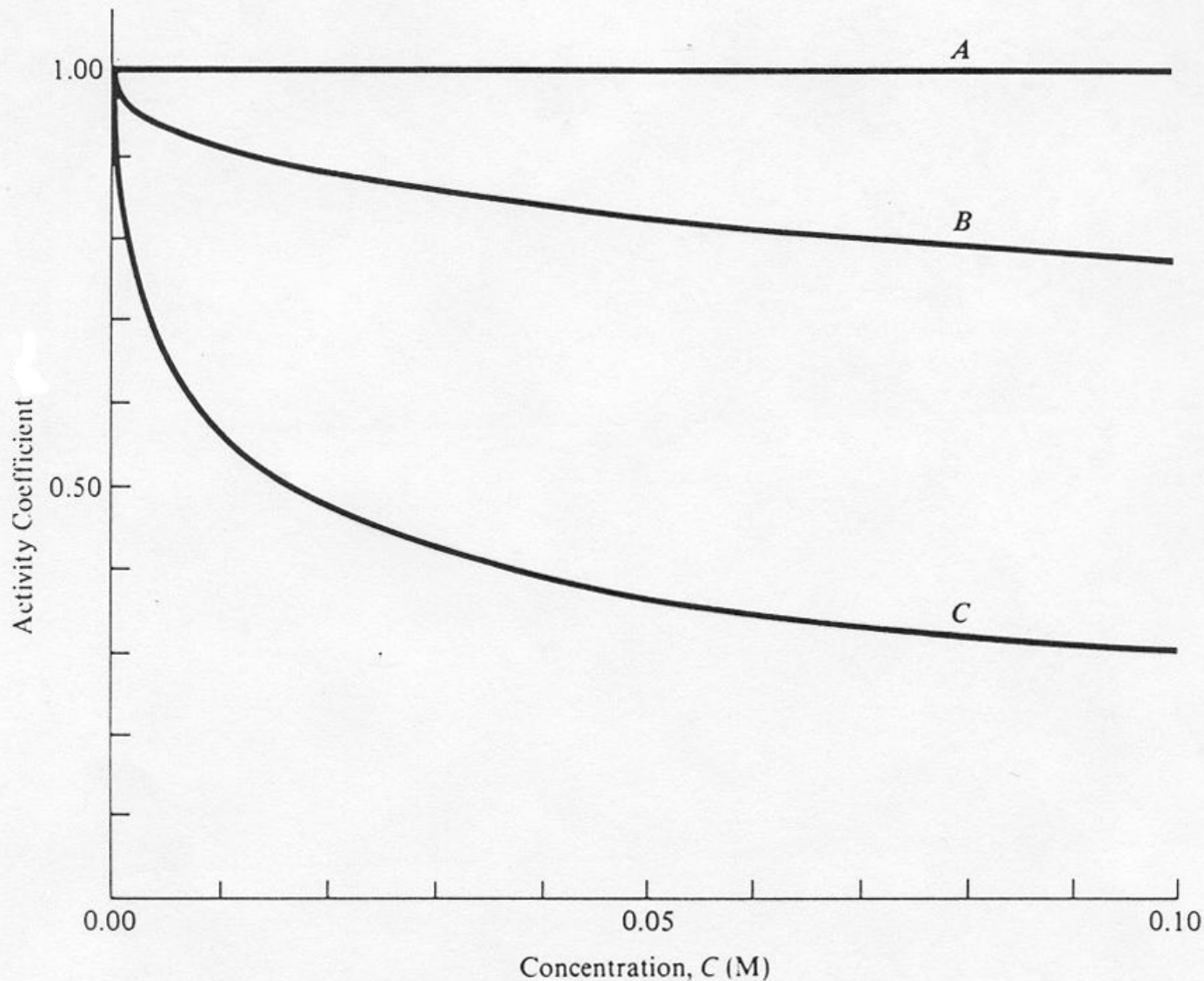


Comparison of
Davies Equation
& Extended
Debye-Huckel
for monovalent
Ions

Morel & Hering 1993



Activity Coefficient vs. Conc., Monovalent & Divalent Systems



Activity Coefficient vs. Conc., Ideal, Monovalent & Divalent Systems

(Kennedy 1990)

FIGURE 4-2 Activity coefficient as a function of concentration in the solution: (A) ideal solution for which $\gamma = 1.00$ at all concentrations; (B) activity coefficient for Na^+ in NaCl solutions; (C) activity coefficient for Ca^{2+} in CaCl_2 solution.

Activity
vs. Conc., Ideal,
Monovalent & Divalent
Systems

(Kennedy 1990)

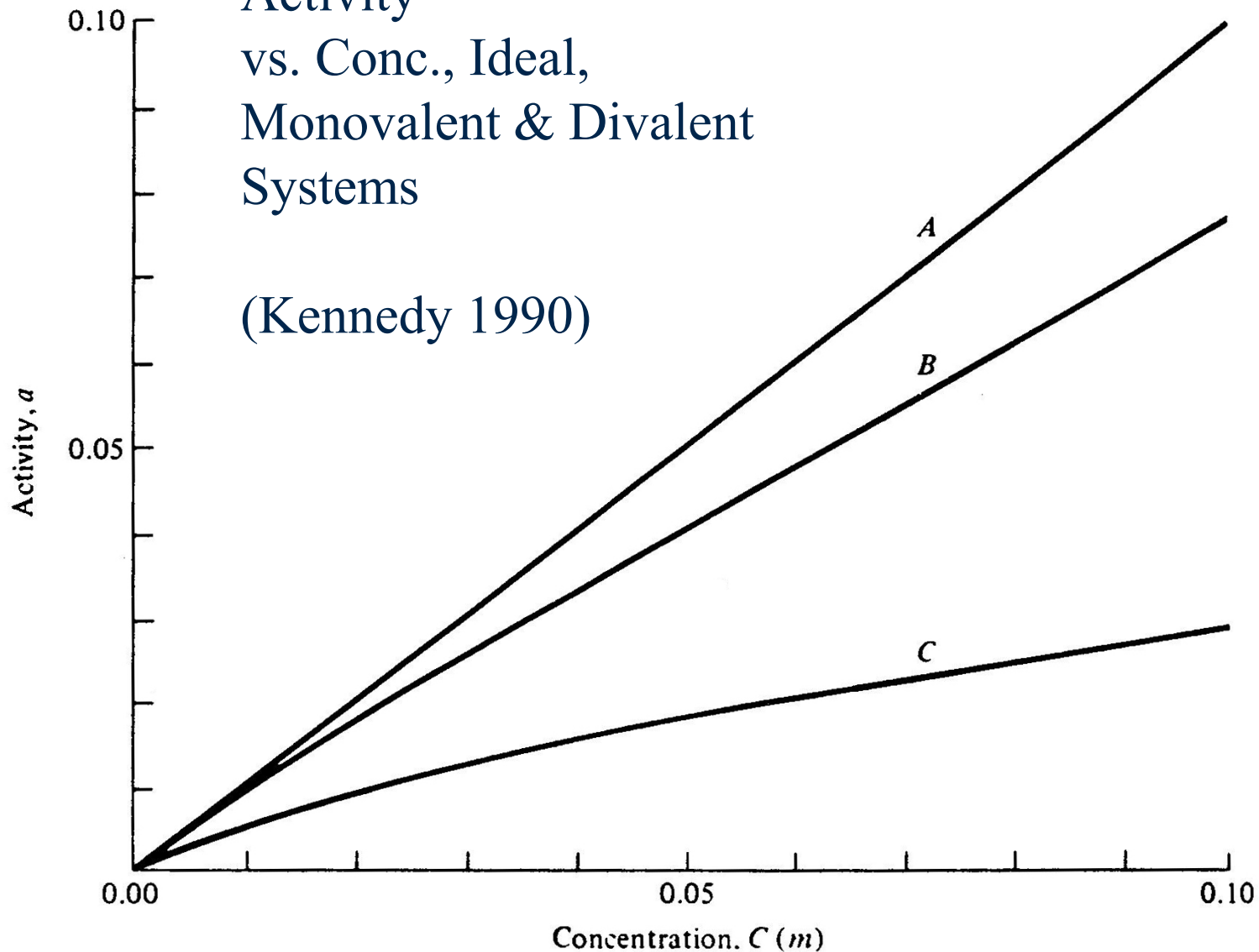


FIGURE 4-1 Activity as a function of concentration: (A) ideal solution for which $a = C$; (B) Na^+ activity in NaCl ; (C) Ca^{2+} activity in CaCl_2 .

Putting It All Together

Calculate ionic strength from concentrations of all ions in solution using $I = 0.5 \sum Z^2 m$

Use Davies Equation to calculate activity coefficients for all ions of interest ($Z = 1, 2, 3, 4$)

$$\ln \gamma_{\pm} = - A Z^2 [I^{0.5}/(1 + I^{0.5}) - 0.2 I]$$

Calculate activity of the ions of interest using their concentrations and activity coefficients

$$a = [i] \gamma$$

Example: pH of SW

pH is defined as the negative
logarithm of the hydrogen ion activity

$$\text{pH} = -\log a_{\text{H}^+}$$

At a typical ionic strength of seawater $I = 0.7$

From Davies Equation H^+ activity coefficient

$$\ln \gamma = -A Z^2 [I^{0.5}/(1 + I^{0.5}) - 0.2 I]$$

If $Z = 1$ & $A = 1.17$ then $\ln \gamma = -0.37$ & $\gamma = 0.69$

Example: pH (cont.)

If a typical seawater pH is 8.2

Then H^+ activity is $1 \times 10^{-8.2}$ or $6.31 \times 10^{-9} \text{ M}$

From $\mathbf{a} = [\mathbf{i}]\gamma$ or $a_{H^+} = [H^+]\gamma_{H^+}$ & calculated $\gamma = 0.69$

$$6.31 \times 10^{-9} \text{ M} = [H^+] \times 0.69$$

$$[H^+] = 9.14 \times 10^{-9} \text{ M}$$

Activity of H^+ is 31% lower than it's concentration

Effectiveness of H^+ is 31% lower due to crowding

This phenomenon is greater for divalent ions