Water

Lecture by Jens Daniel Müller
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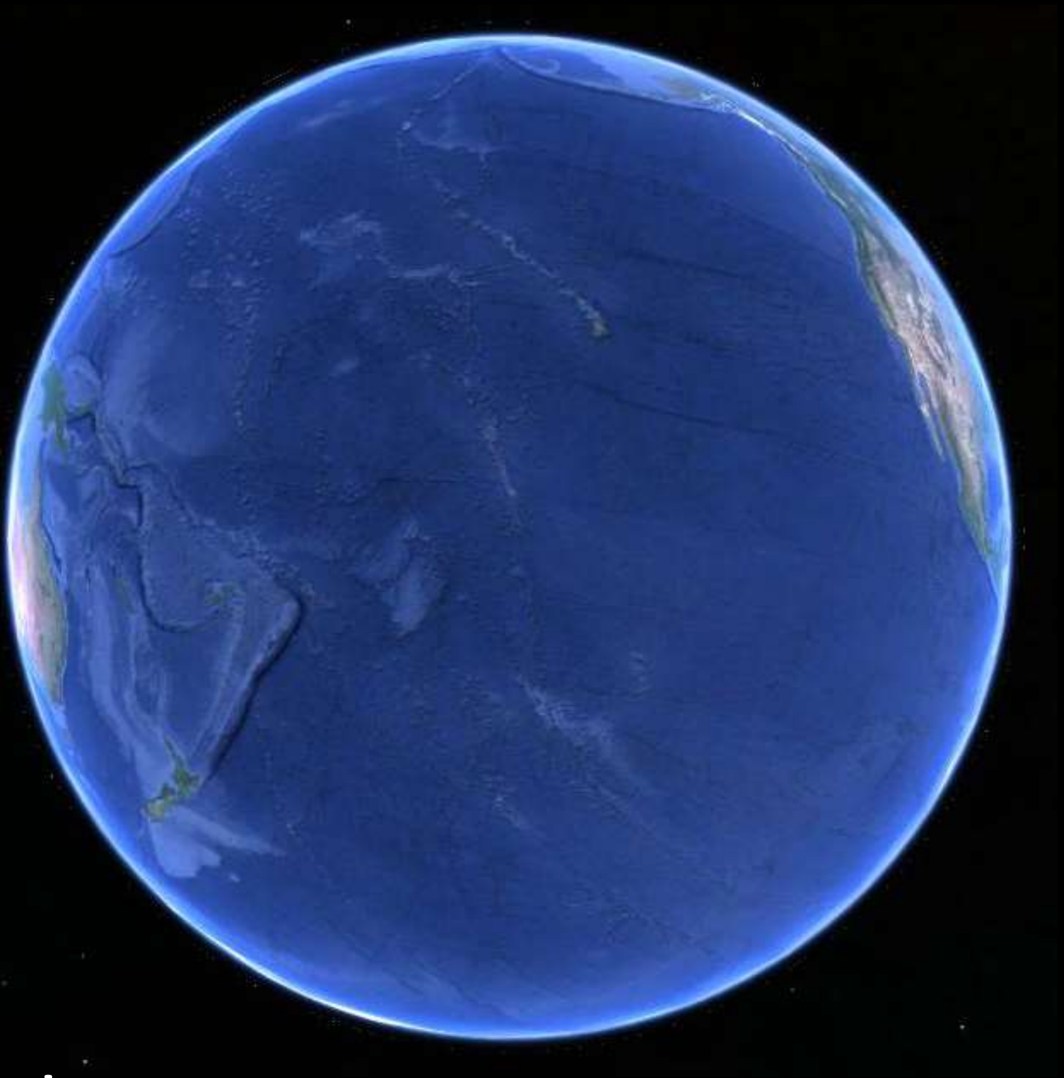
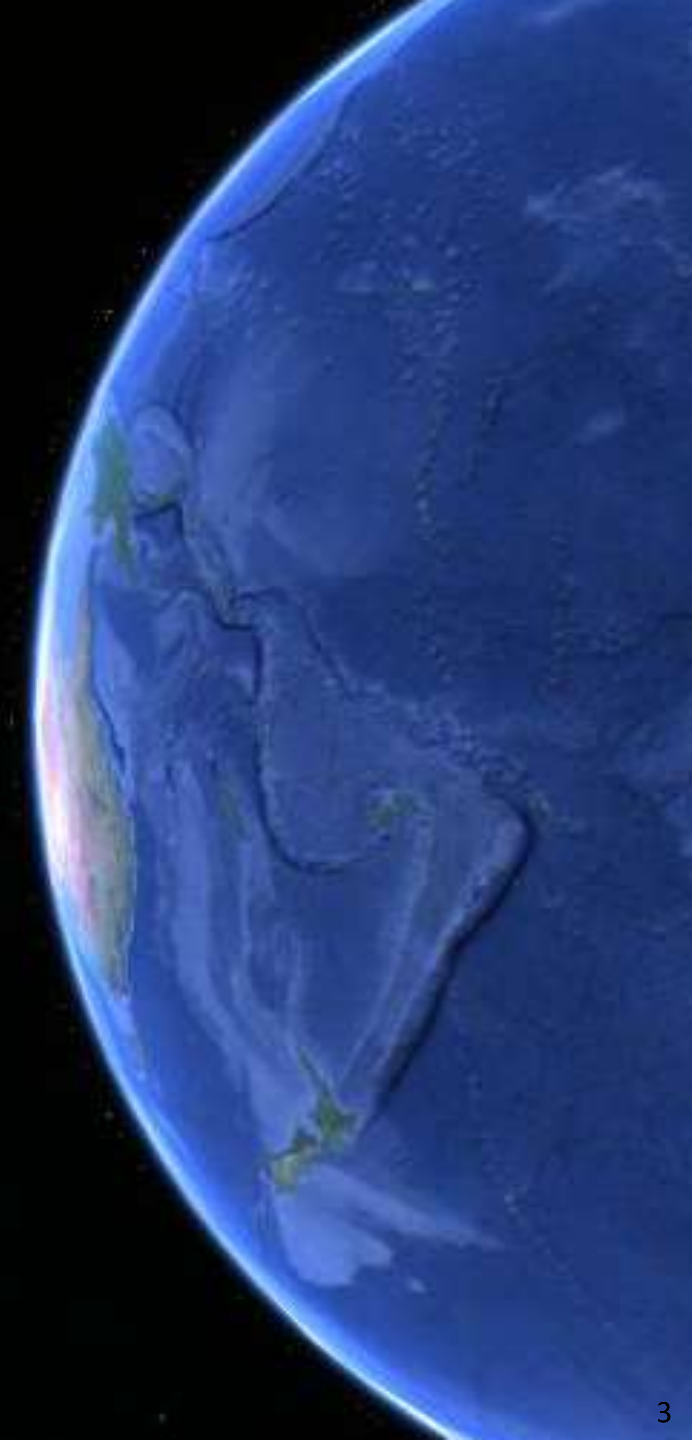
Water covers 71% of the Earth‘s surface…



…and plays a central role in controlling its climate and conditions for live!

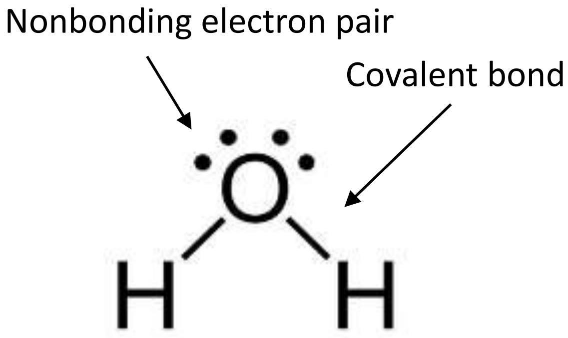
Outline

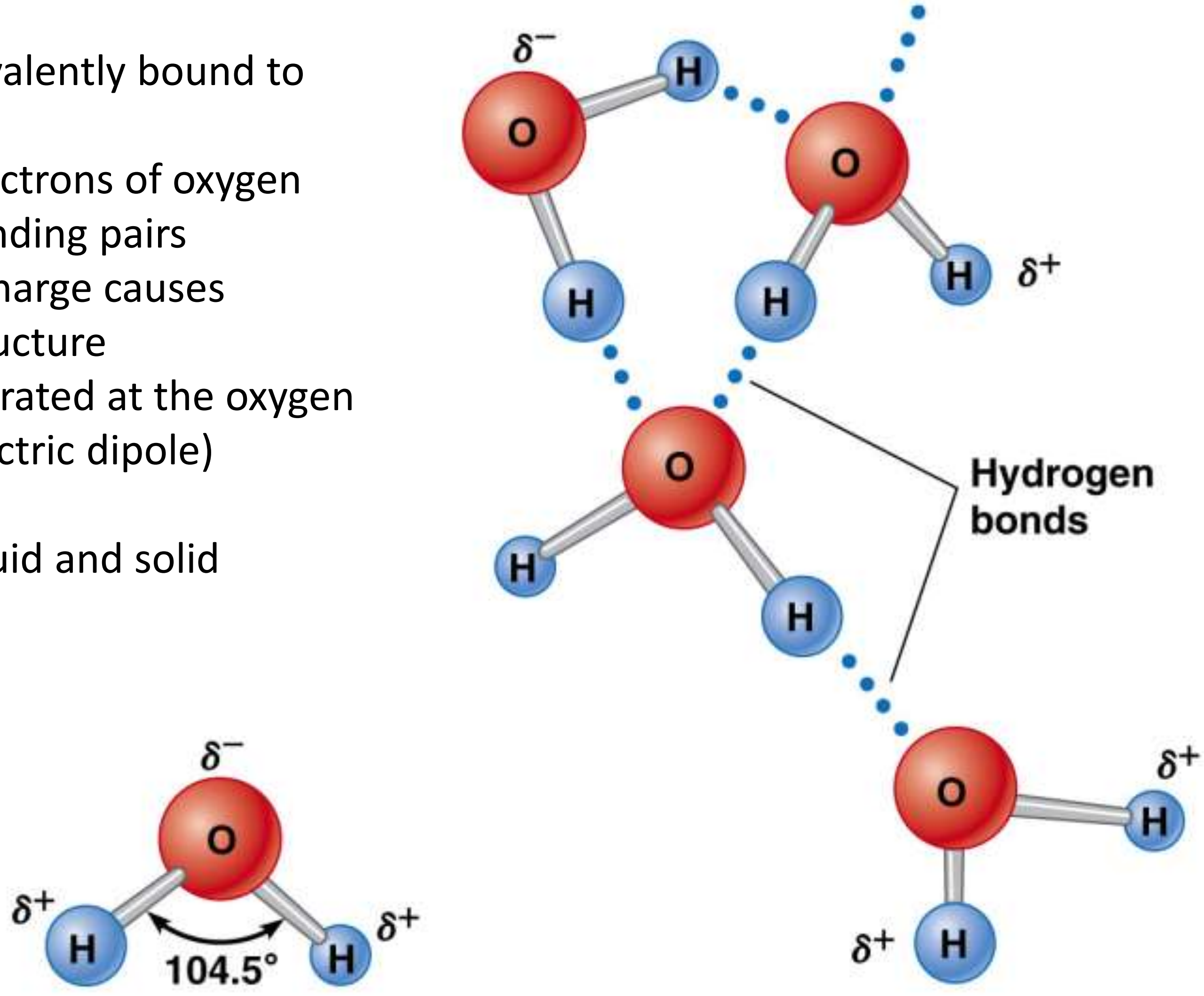


- Physico-chemical properties of water
- Density anomaly
  - The temperate lake
- Melting, evaporation, heat transport
  - Water as a climate regulator
- From pure water to oceans
  - Origin of salt
  - Ocean conveyor belt
- Speciation in water
  - Activity vs concentration
  - pH-dependence
  - Phosphoric acid

The water molecule

- Two hydrogen atoms covalently bound to central oxygen atom
- 4 out of 6 outer-shell electrons of oxygen organized into 2 non-bonding pairs
- Repulsions of negative charge causes distorted tetrahedral structure
- Negative charge concentrated at the oxygen end of the molecule (electric dipole)
- Dipole-dipole attraction
- Hydrogen bonding in liquid and solid





(a) Polarity of water molecule

(b) Hydrogen bonding between water molecules

Water: From solid to liquid

Ice (solid)

- Hexagonal puckered rings

Melting

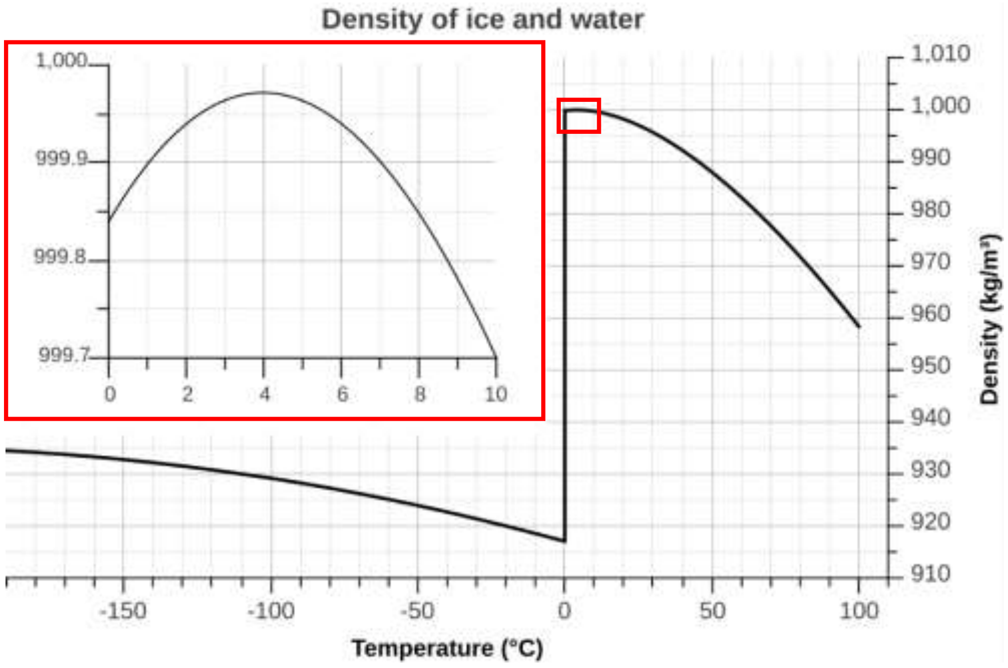
- 12% of hydrogen bonds break

➢ Density ice < water (at 0°C)*

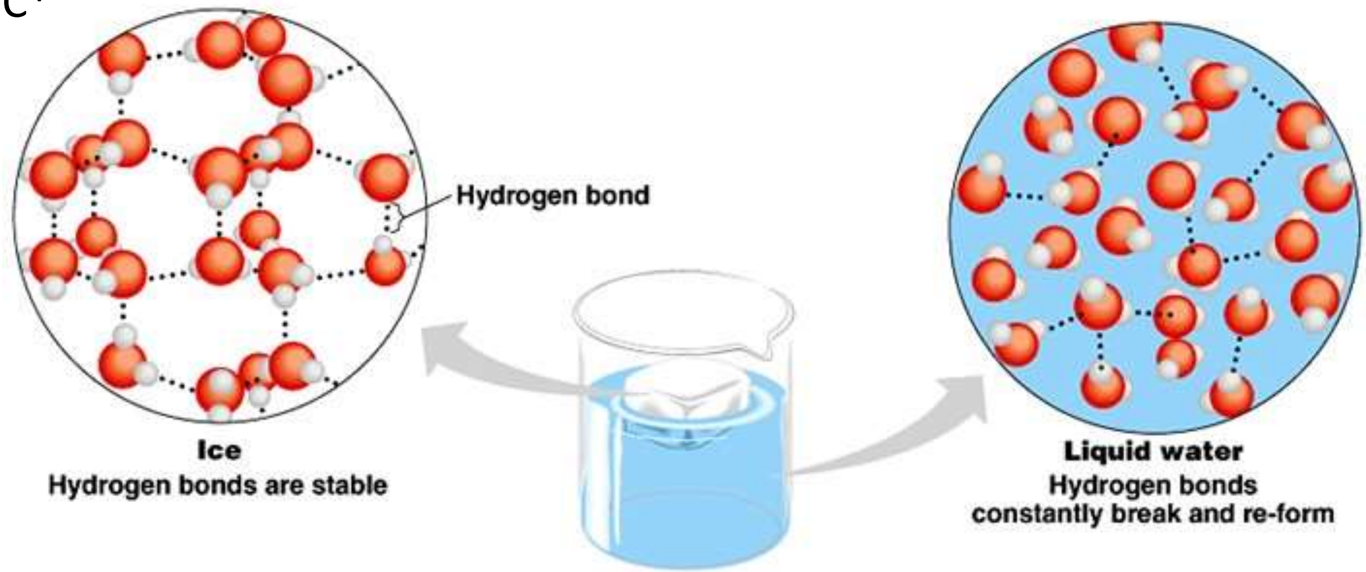
Water (liquid)

- While heating to 100°C
  - Another 8% hydrogen bonds break (increasing density)
  - Kinetic energy of molecules increases (decreasing density)

➢ Highest density ~4°C*

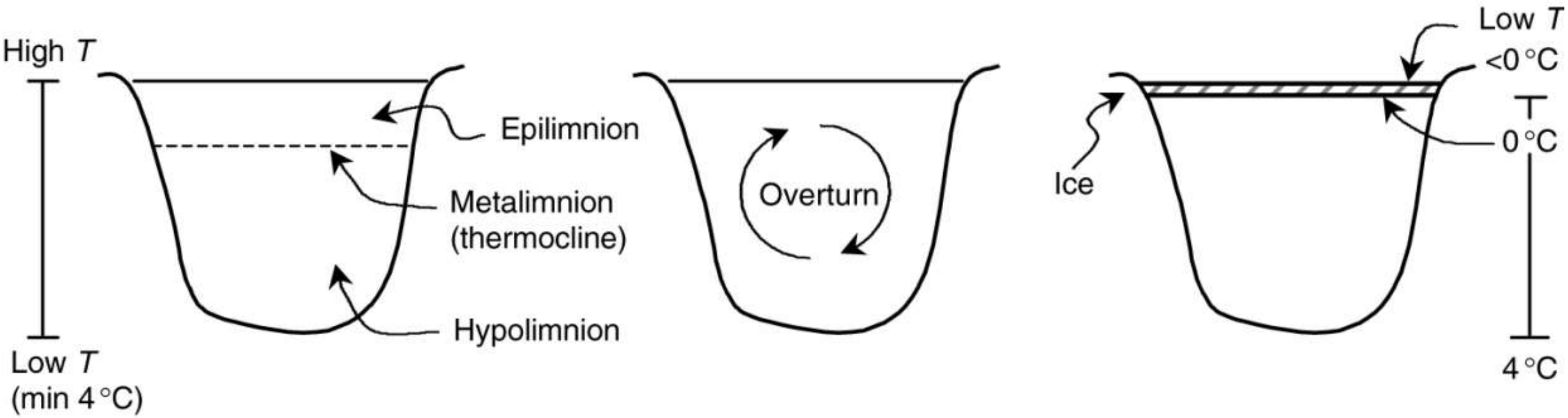


*density anomaly



Consequences of the density anomaly: Seasonality in lakes in temperate regions

- Thermal stratification after cooling below 4°C at surface
- Surface ice formation
- Non-frozen deeper water layers



Warm climate (summer)

Solar radiation penetrates the epilimnion, stimulating algal photosynthesis and producing oxygen.
Little solar radiation reaches the hypolimnion; there is no photosynthesis, but bacterial decomposition of organic matter causes depletion of oxygen.

Cool weather (autumn)

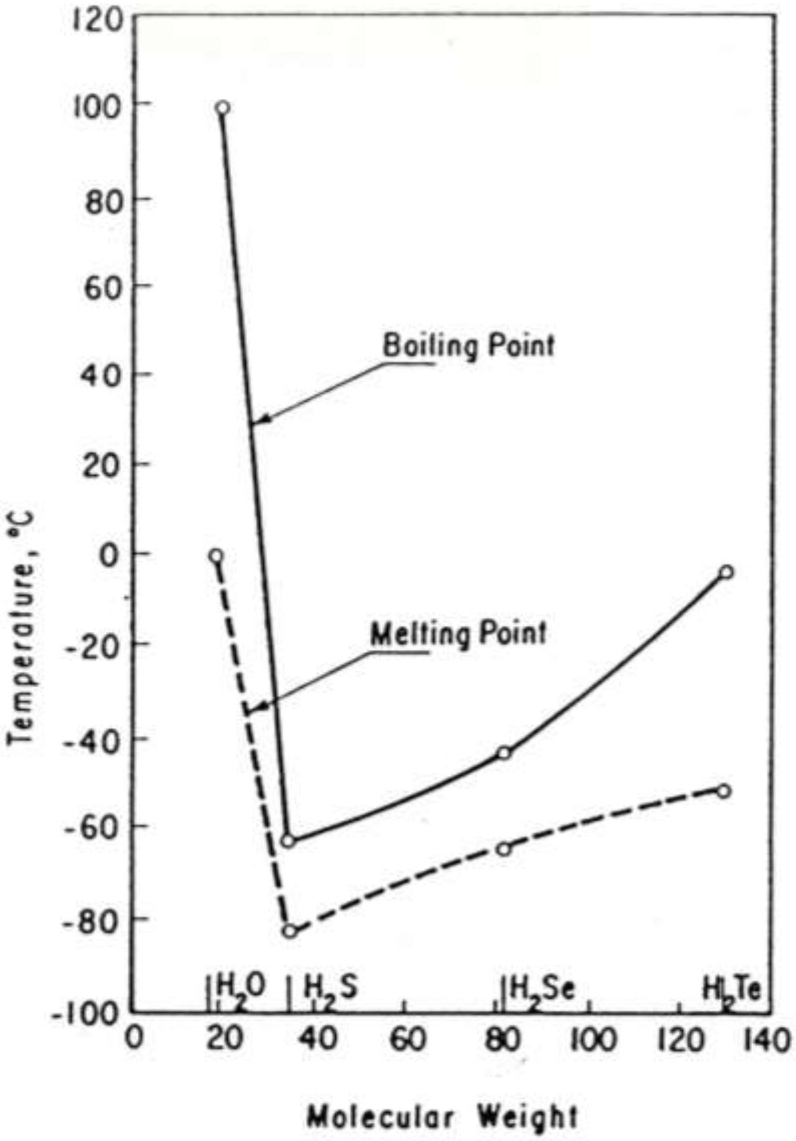
Cooled surface water sinks to the bottom, forcing bottom water upwards, creating a homogeneous (T and nutrients) environment.

Cold weather (winter)

Ice forms on the surface; temperature relatively uniform below ice layer.

How would that compare to the ocean…?

Water - changing the state of matter



- Drastically increased melting and evaporation points of water compared to hydrogen compounds of heavier elements, due to hydrogen bonding
- High heat capacity

➢ A lot of energy required to heat and evaporate water

➢ Effective climate regulator

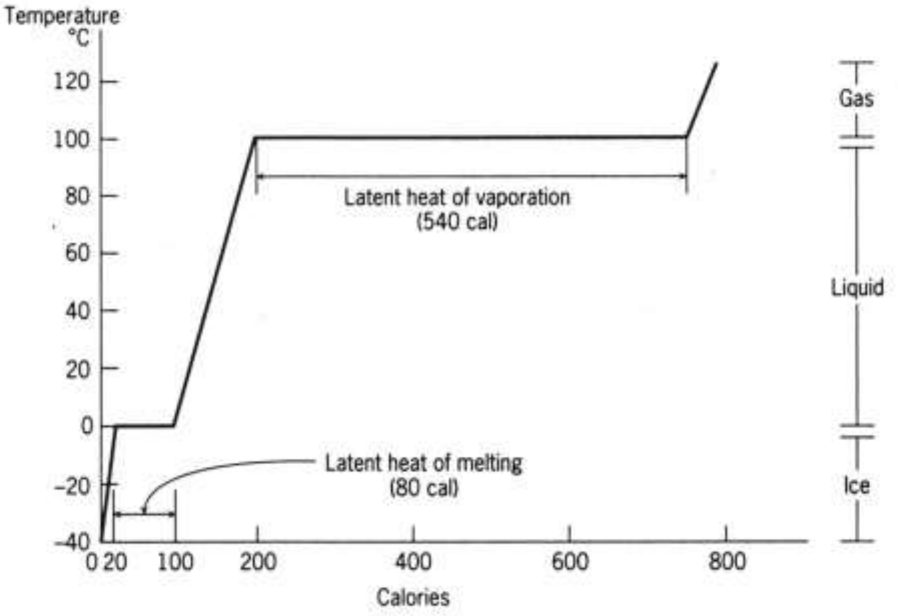


FIGURE 2.9. The phase transitions of water as caused by changing heat content. Slopes of the lines indicate heat capacity.

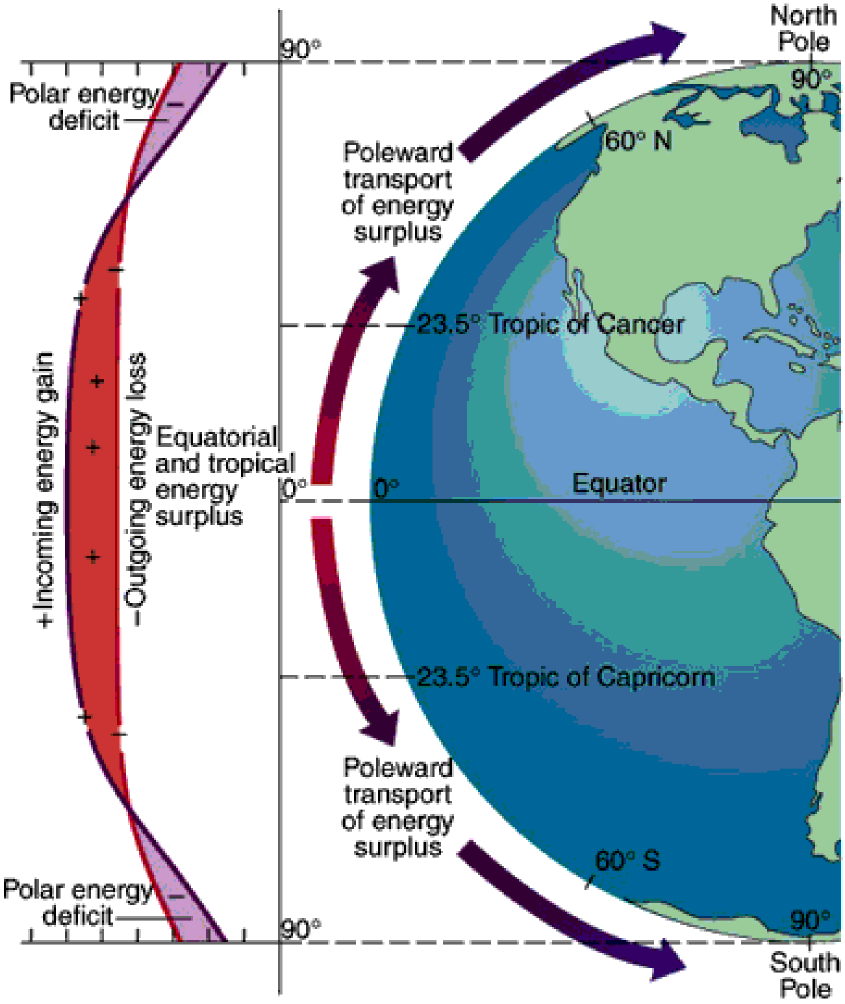
Water as an effective climate regulator

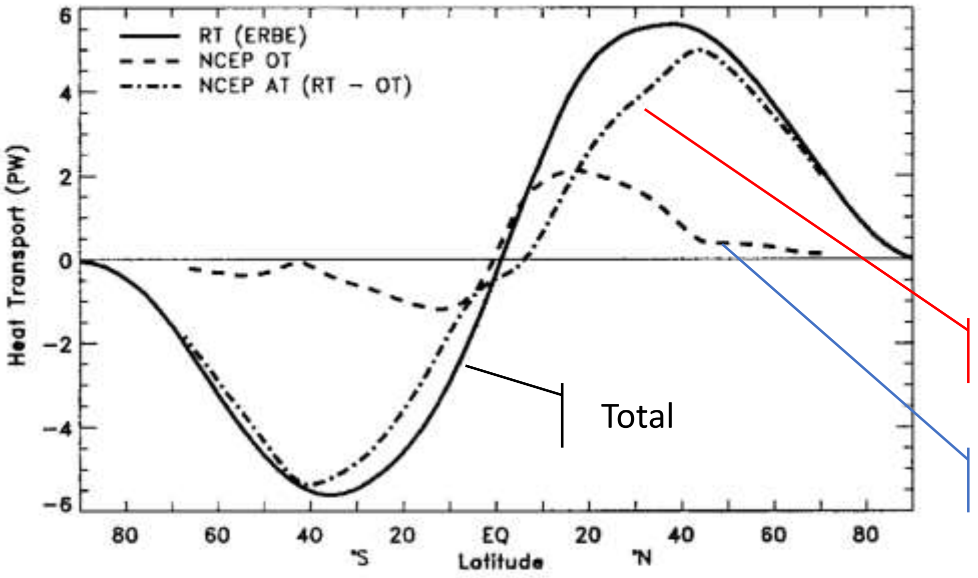
Presence of water reduces temperature gradients between:

- Poles and equator
- Summer and winter
- Day and night

Weather systems and ocean currents result from constant flow of heat from the tropics to the poles:

- Latent heat flux: evaporation and precipitation (change of state)
- Sensible heat flux: surface ocean currents (change of temperature)





Atmosphere

Ocean

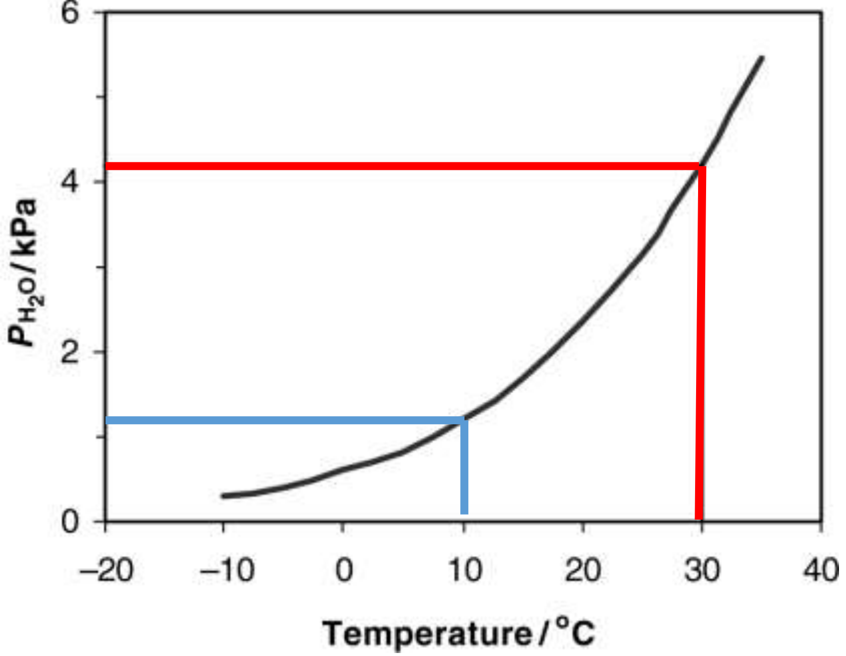
Trenberth & Caron (2001)

Sample calculation: Latent vs sensible heat fluxes

How does the latent heat flux of water vapor in the atmosphere compare to the sensible heat flux by surface ocean currents?

Required information:

Saturation vapor pressure H_2O



How much water is in air?

$P_{H2O,real}$ = HR /100 x $P_{H2O,sat}$

pV = nRT

R = 8.314 J mol^{-1} K^{-1}

Molar mass (H_20) = 18.02 g/mol

How much heat is realized by precipitation?

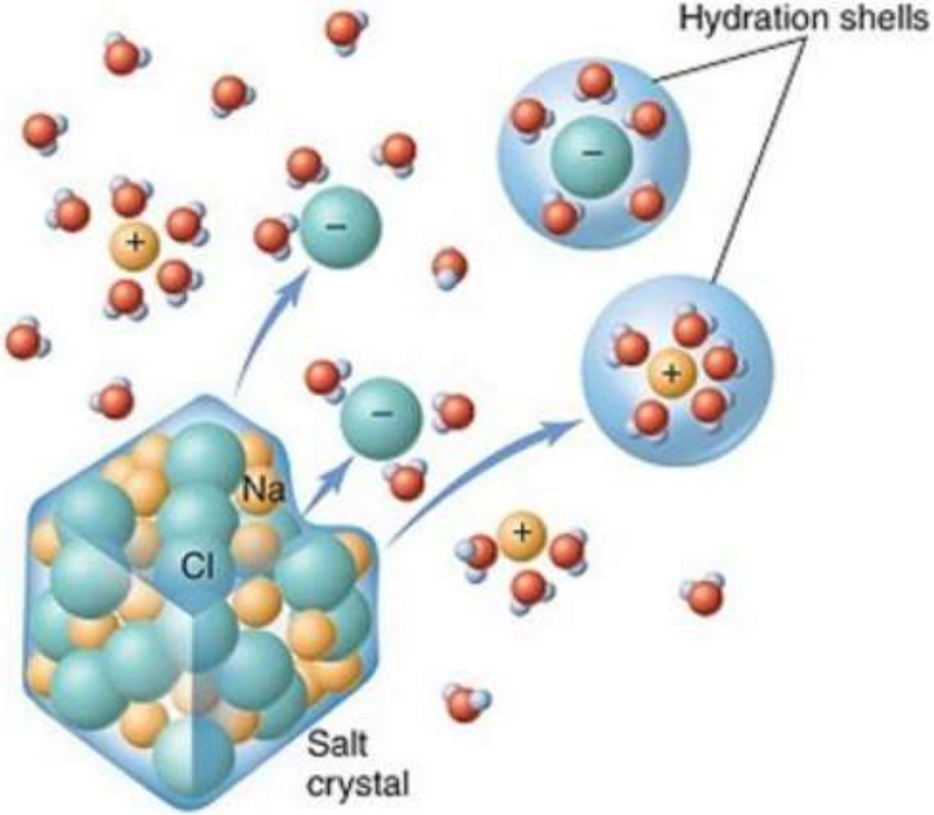
Latent heat of vaporation (H_20) = 2258 J/g

(compare previous slide, 1 cal = 4,1868 J)

How much water must be cooled to transport the same amount of energy?

Heat capacity (seawater) = 3.9 $Jg^{-1}K^{-1}$

Water as a solvent



Water as a solvent

- High dipole moment and polarity cause high solubility of many ionic substances
- Hydration determined by charge density of ions
- High solubility results in accumulation of salts in seawater

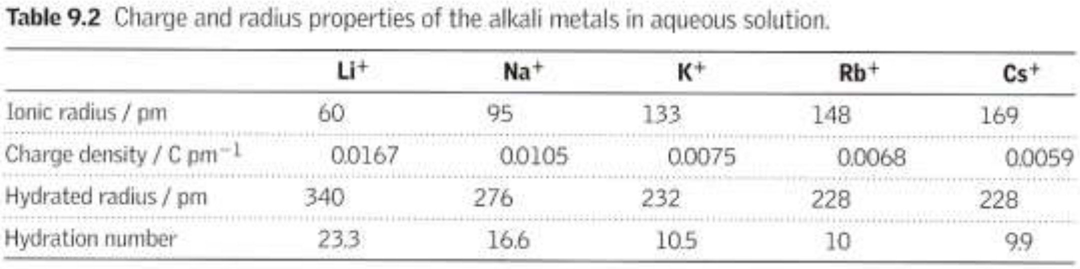
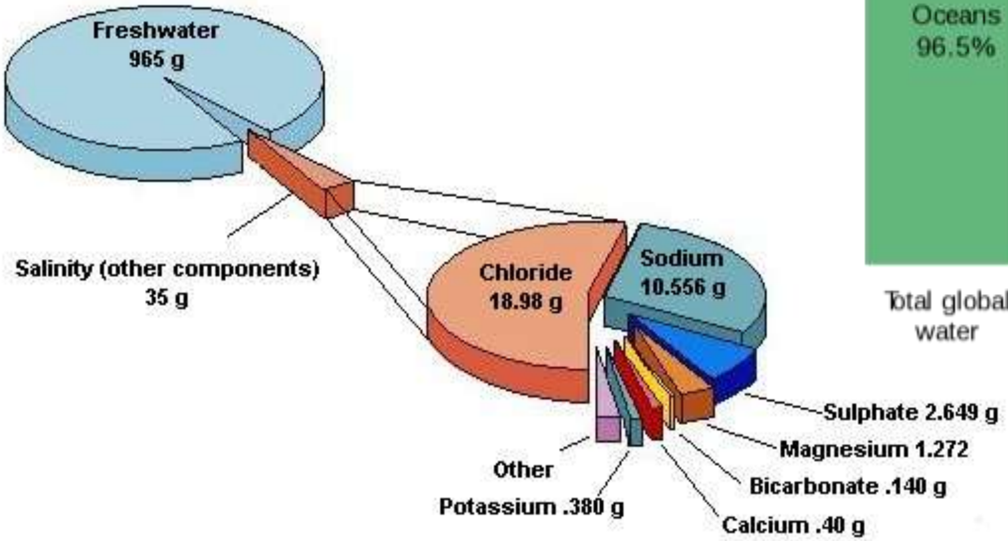


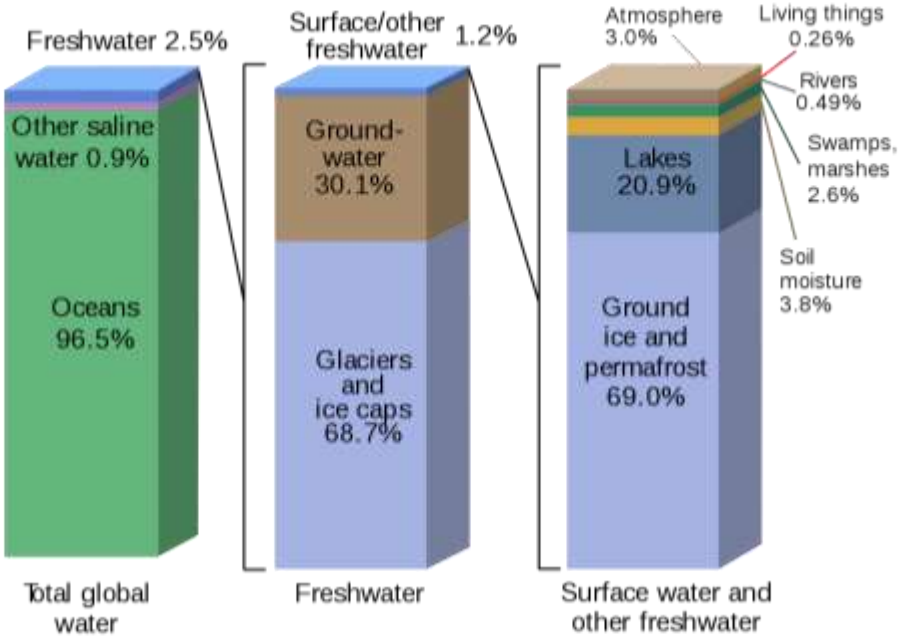
Table 9.2 Charge and radius properties of the alkali metals in aqueous solution.

	Li^+	Na^+	K^+	Rb^+	Cs^+
Ionic radius / pm	60	95	133	148	169
Charge density / C pm^{-1}	0.0167	0.0105	0.0075	0.0068	0.0059
Hydrated radius / pm	340	276	232	228	228
Hydration number	23.3	16.6	10.5	10	9.9

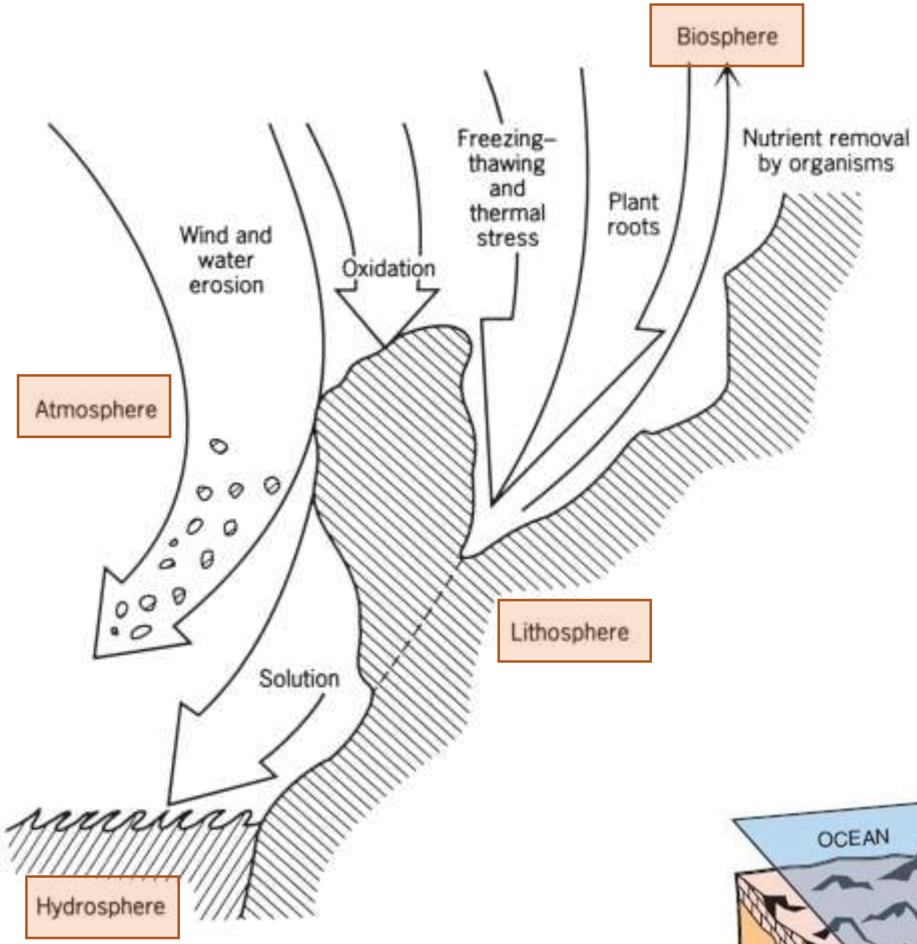
Oceanic seawater composition



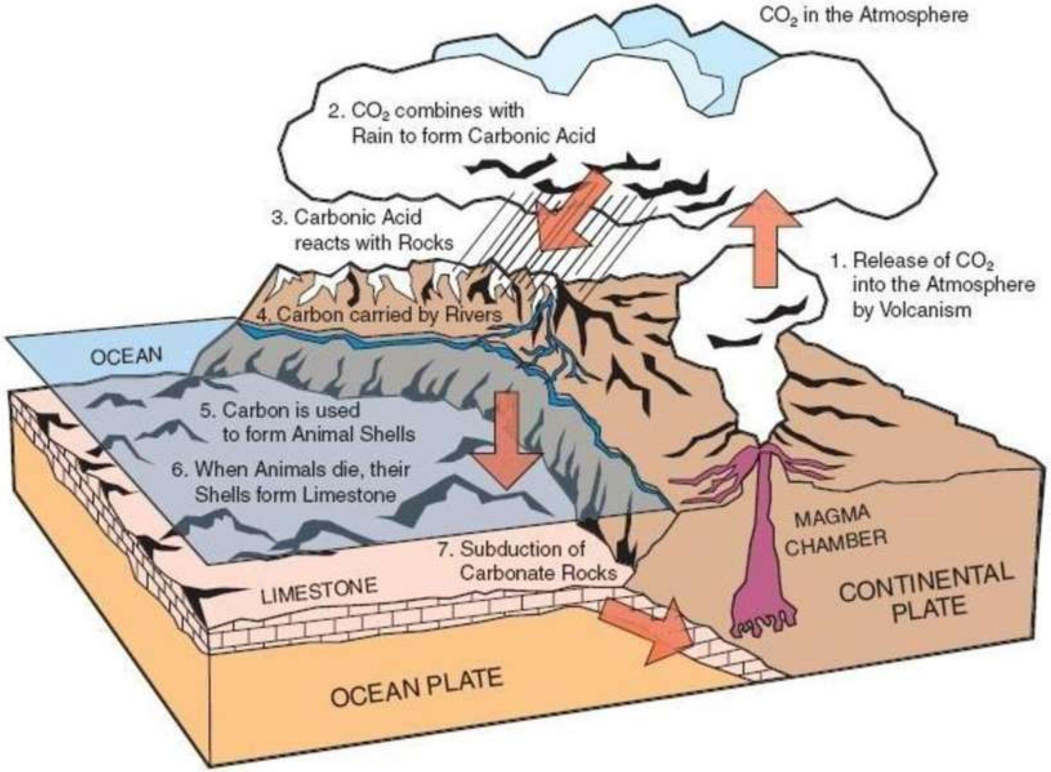
Earth's water reservoirs



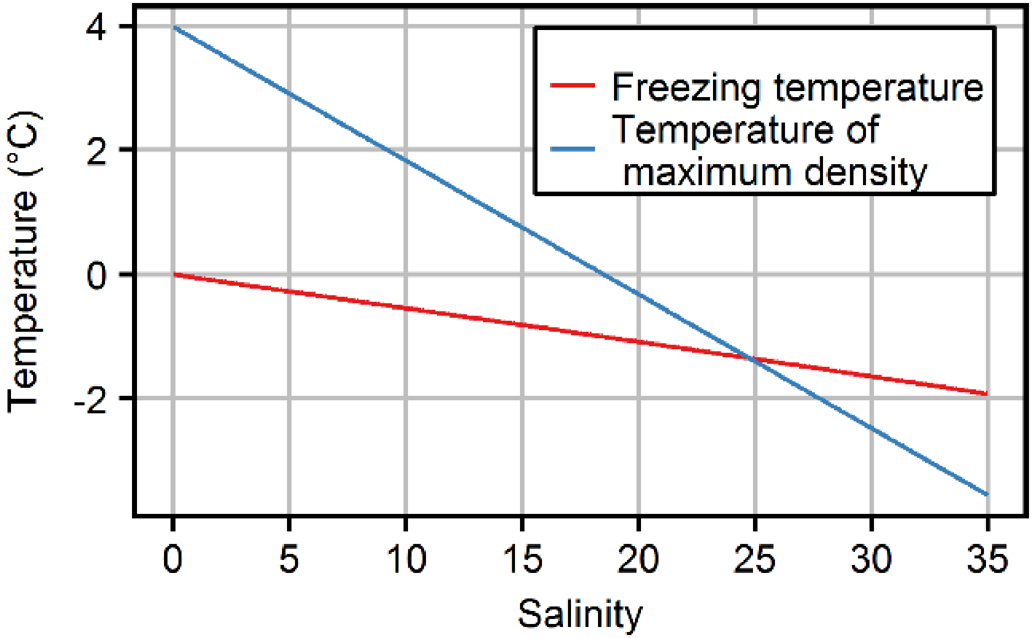
Source of salt: Continental weathering



- Water -> physical leaching
- Facilitated by vegetation and other associated organisms (e.g., bacteria, fungi, etc)
- Anthropogenically sensitive!



Consequences of salts in water



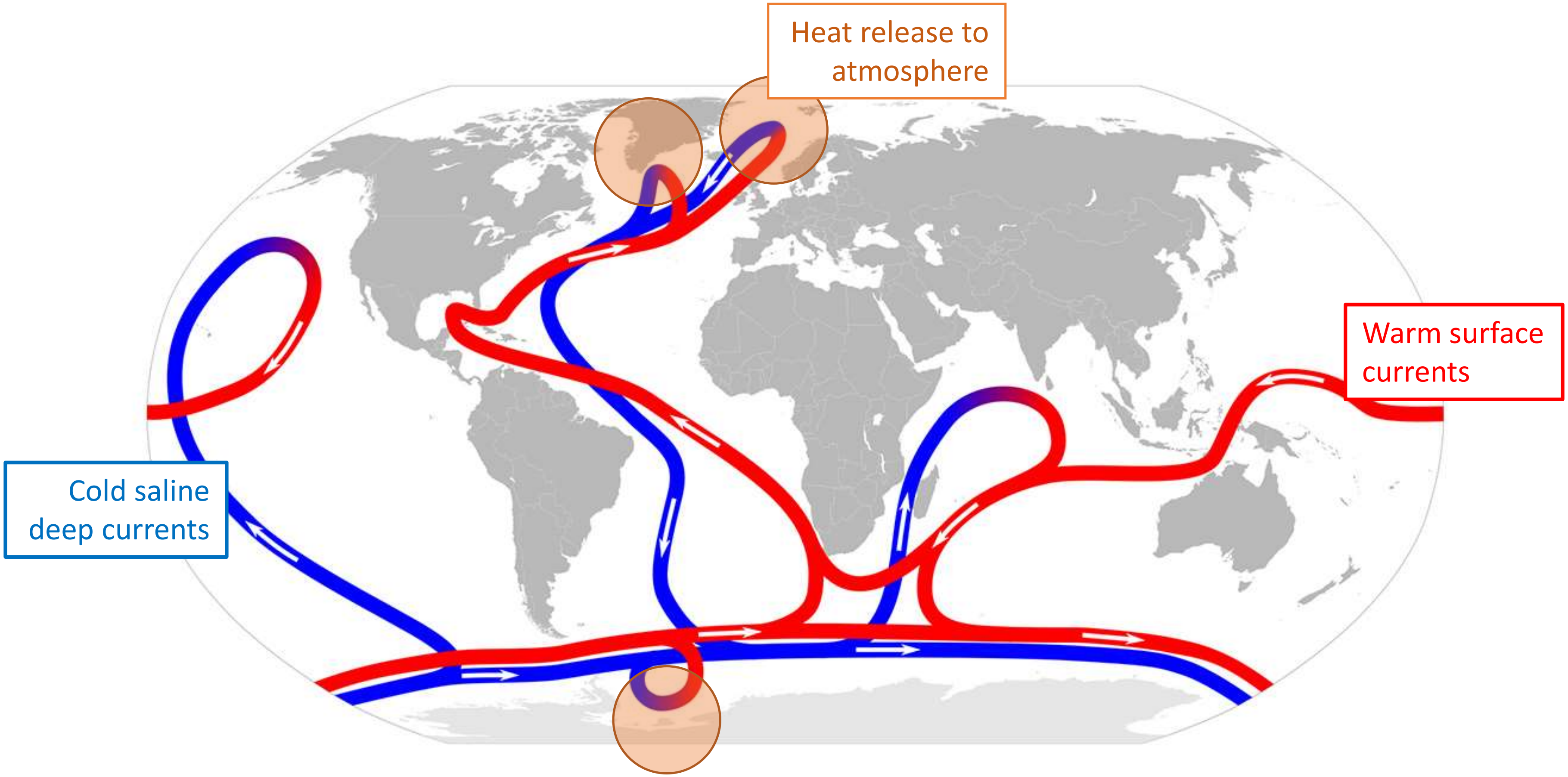
Watch out:

The presence of ions in water (expressed as salinity) changes the relation of the freezing point and the temperature of maximum density!

Does this have environmentally relevant consequence?

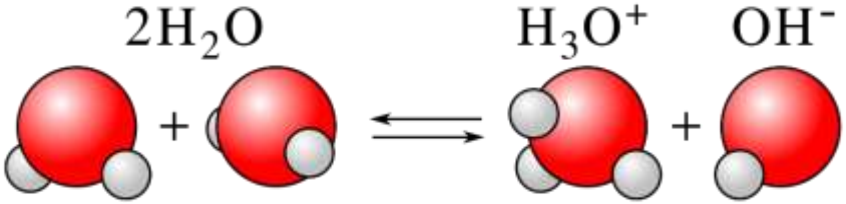
Thermohaline circulation: The Global Ocean Conveyor Belt

- High latitude global ocean: Cold water (as cold as -1.9 °C) sinks due to high density
- ➢ Deep convection allows to maintain heat transport
- Supported by increasing salinity during ice formation
- Would not be possible in a “freshwater ocean” due to density anomaly



Speciation of substances in water

- Self-ionisation and amphoterism of water
- pH = -log H_30^+
- Neutral pH: $[H_3O^+] = [OH^-]$



- Equilibrium reactions depend on temperature and chemical environment

Ionic product of water

$K_w = [H_3O^+] \times [OH^-]$

25 C: $K_w = 1.0 \times 10^{-14}$

- ➢ pH = 7.0

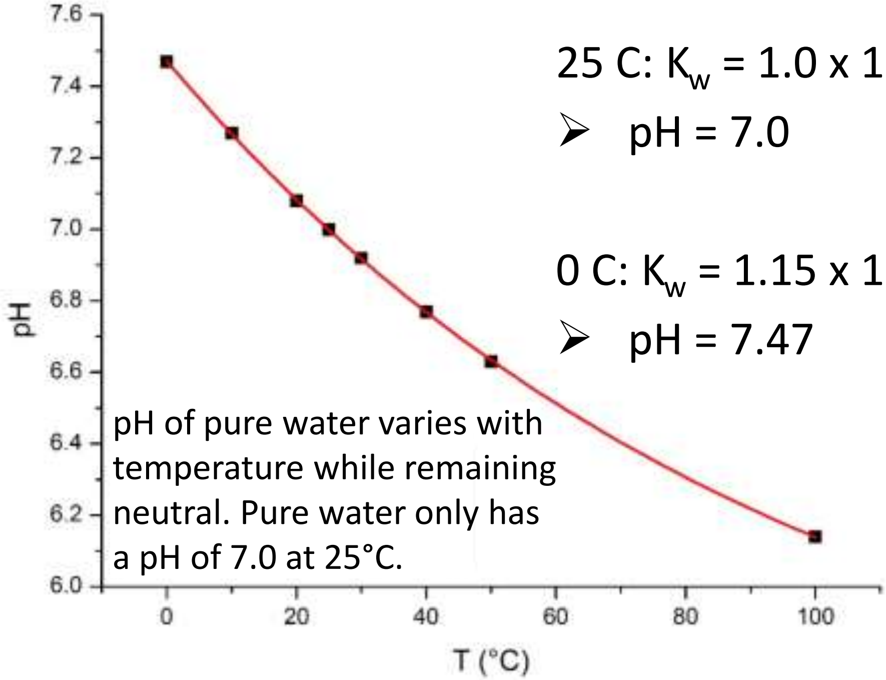
0 C: $K_w = 1.15 \times 10^{-15}$

- ➢ pH = 7.47

- Watch out: concentration units!
  - mol/L
  - mg/kg
  - mol/kg
  - Often useful for element under consideration

(18mg/L NH_4^+ ~ 62 mg/L NO_3^-

=> **14 mg/L N)**



pH of pure water varies with temperature while remaining neutral. Pure water only has a pH of 7.0 at 25°C.

Speciation in water: Example phosphoric acid – a triprotic acid

- Chemical properties of elements and compounds depend on speciation and therefore on chemical environments
- First approximation: activity = concentration
- Often useful: dependence on key parameter such as pH

$$H_3PO_4 \rightleftharpoons H_2PO_4^- \rightleftharpoons HPO_4^{2-} \rightleftharpoons PO_4^{3-}$$

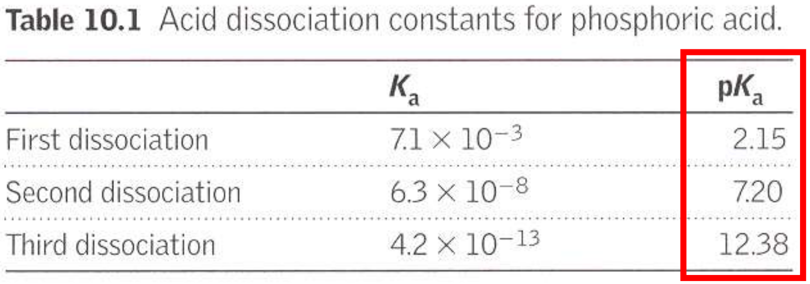
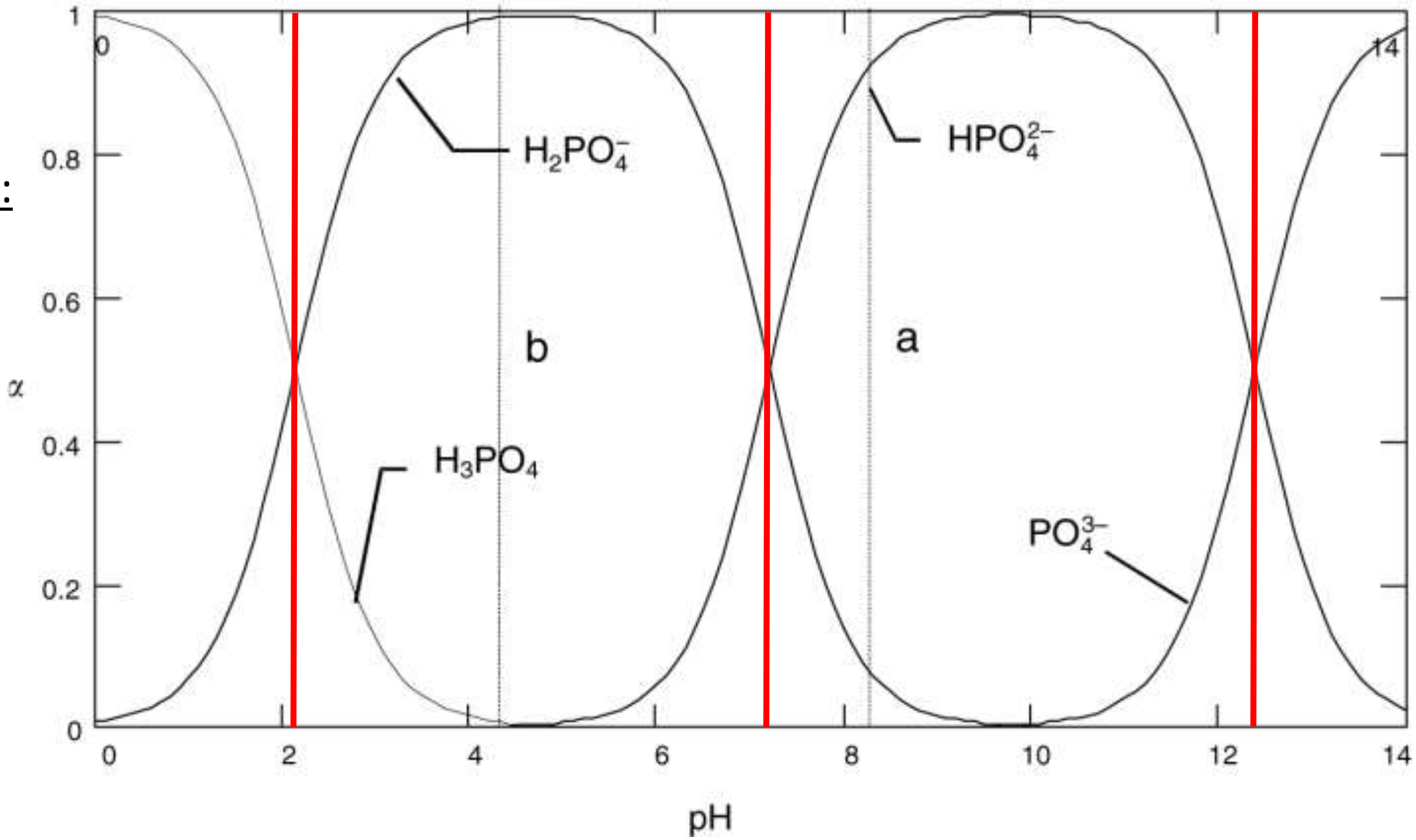


Table 10.1 Acid dissociation constants for phosphoric acid.

	K_a	pK_a
First dissociation	7.1×10^{-3}	2.15
Second dissociation	6.3×10^{-8}	7.20
Third dissociation	4.2×10^{-13}	12.38

<u>Speciation diagram:</u>
α: Fraction of each phosphate species relative to total phosphate (sum of all species)



Interactions between ions in solution: Activity or the “effective concentration”

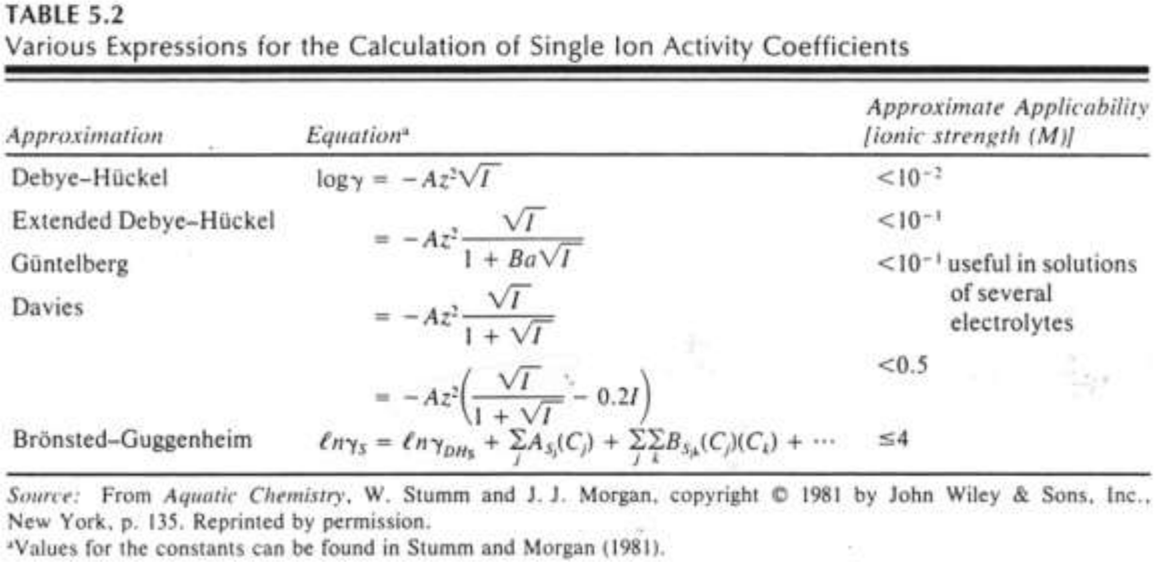


TABLE 5.2
Various Expressions for the Calculation of Single Ion Activity Coefficients

Approximation	*Equation*[a]	*Approximate Applicability [ionic strength (M)]*
Debye–Hückel	$\log \gamma = -Az^2\sqrt{I}$	$<10^{-2}$
Extended Debye–Hückel	$= -Az^2 \dfrac{\sqrt{I}}{1 + Ba\sqrt{I}}$	$<10^{-1}$
Güntelberg		$<10^{-1}$ useful in solutions of several electrolytes
Davies	$= -Az^2 \dfrac{\sqrt{I}}{1 + \sqrt{I}}$	
	$= -Az^2\left(\dfrac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I\right)$	<0.5
Brönsted–Guggenheim	$\ell n \gamma_S = \ell n \gamma_{DH_S} + \sum_j A_{S_j}(C_j) + \sum_j\sum_k B_{S_{jk}}(C_j)(C_k) + \cdots$	≤ 4

Source: From *Aquatic Chemistry*, W. Stumm and J. J. Morgan, copyright © 1981 by John Wiley & Sons, Inc., New York, p. 135. Reprinted by permission.

[a] Values for the constants can be found in Stumm and Morgan (1981).

Calculation of single ion activity coefficients

$a_i = \gamma_i \cdot c_i$

A= constant, characteristic of the ion

z = charge of the ion

Ionic Strength: $I = 1/2\ \Sigma c_i \cdot z_i^2$

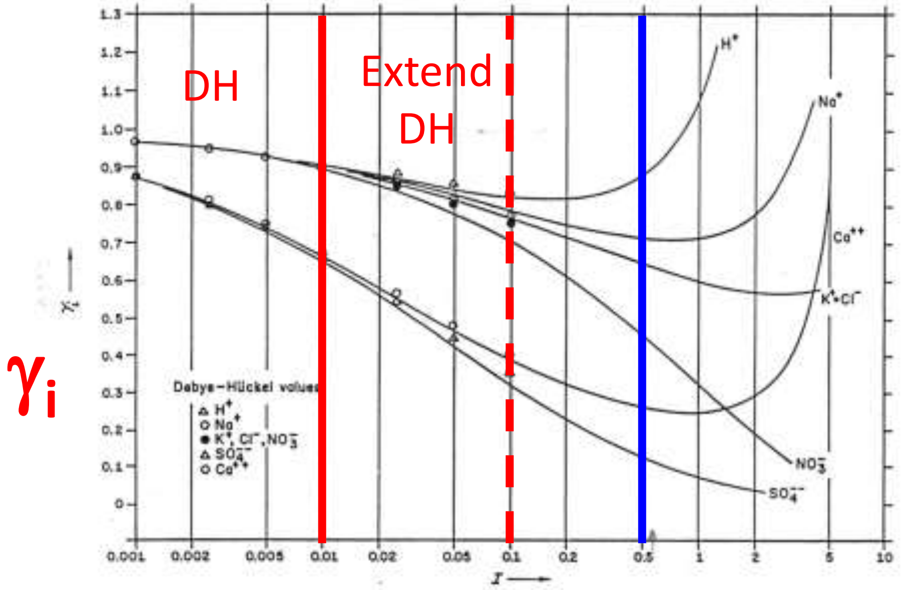


FIG. 2.15. Single ion activity coefficients vs. ionic strength for some common ions. Solid lines represent the values calculated by the mean salt method. Debye-Hückel values were calculated using equation (2.76), with $10^8/\hat{a}_i = 9$ for H^+; 4 for Na^+; 3 for K^+, Cl^-, NO_3^-; 6 for Ca^{++}; and 4 for SO_4^{--}. The Debye-Hückel γ_i values for the monovalent ions converge, within experimental error, for $I < 0.01$.

Speciation of phosphoric acid in different chemical environments

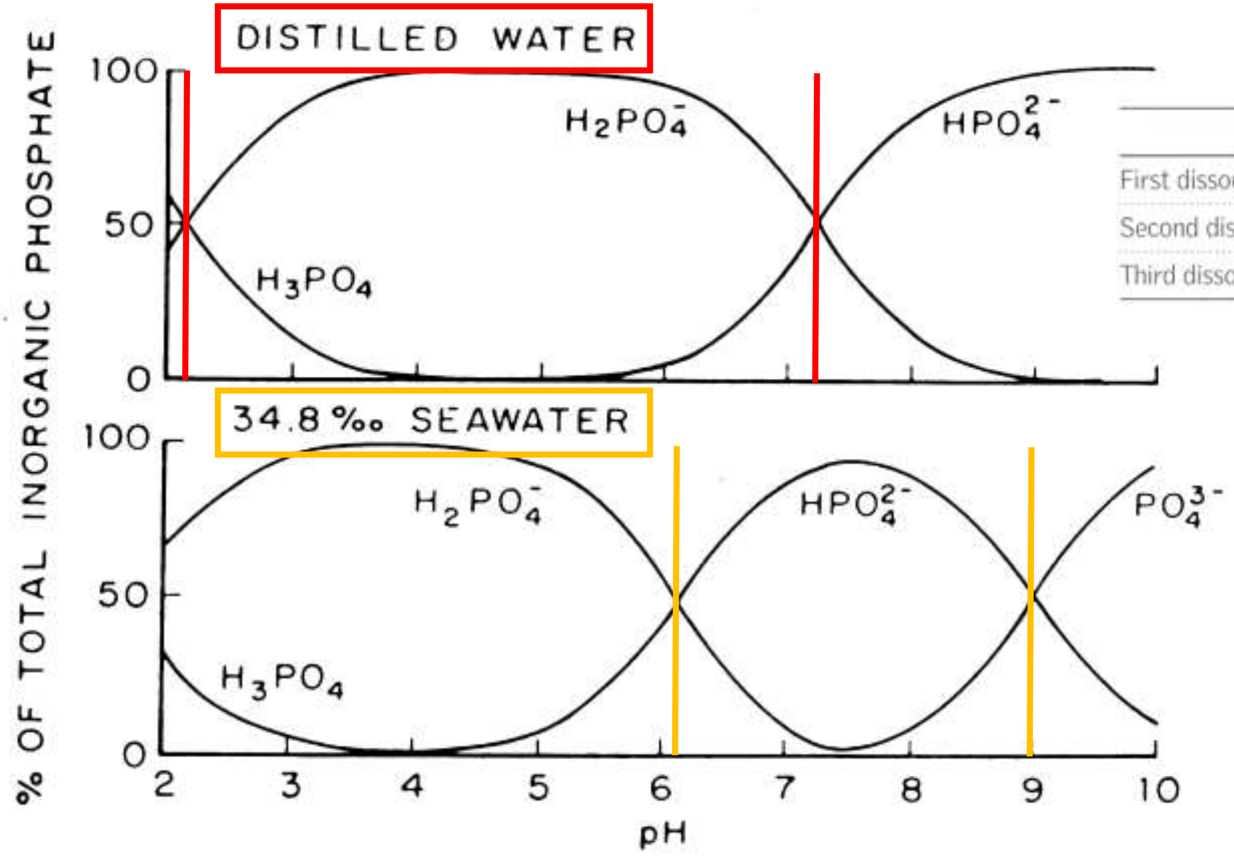


Fig. 14-1 Distribution of phosphoric acid species as a function of pH in distilled water and seawater (Atlas, 1975).

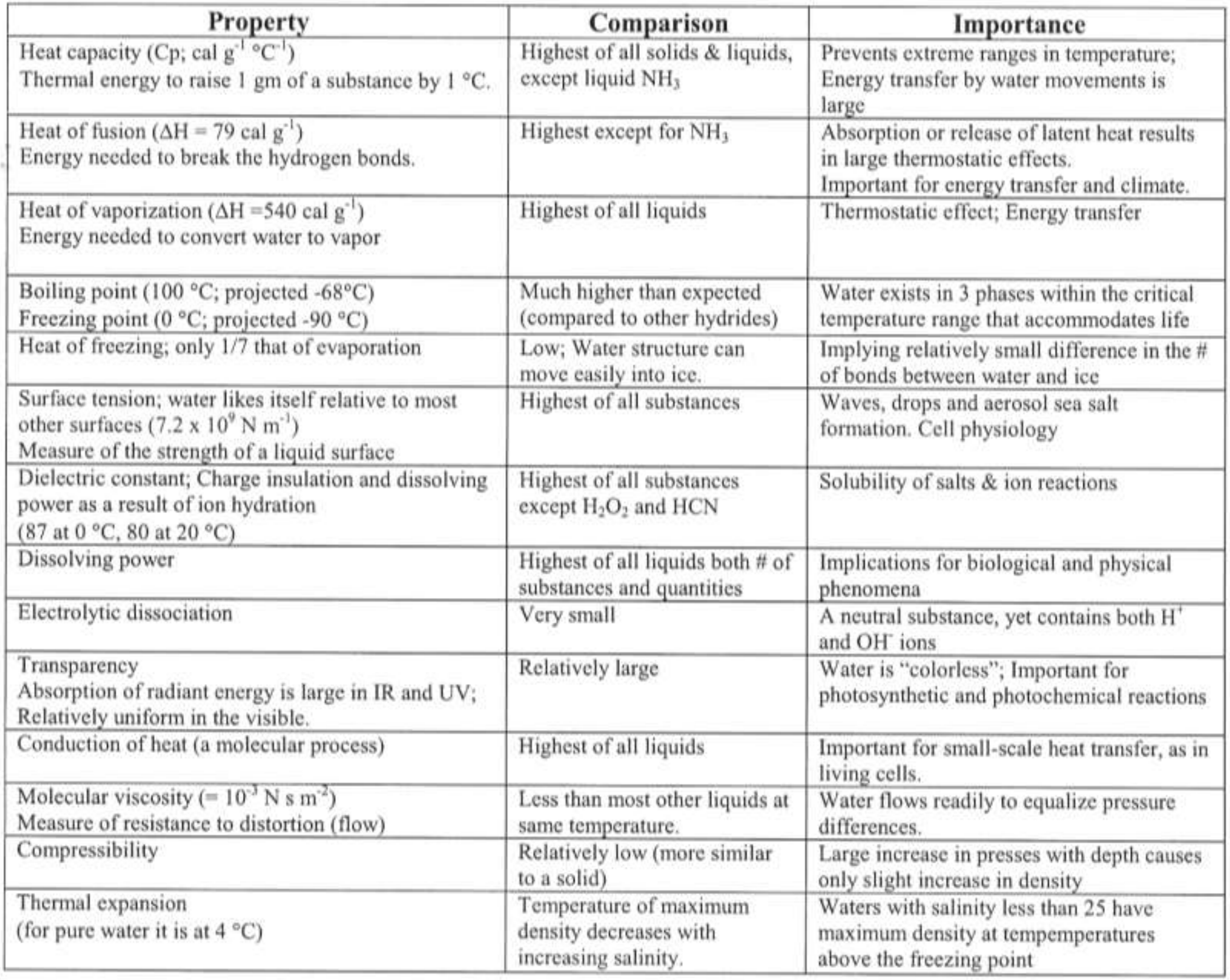
	K_a	pK_a
First dissociation	7.1×10^{-3}	2.15
Second dissociation	6.3×10^{-8}	7.20
Third dissociation	4.2×10^{-13}	12.38

$K_{a1} = 2.4 \times 10^{-2}$ $pK_{a1} = 1.62$

$K_{a2} = 8.8 \times 10^{-7}$ $pK_{a2} = 6.06$

$K_{a3} = 1.4 \times 10^{-9}$ $pK_{a3} = 8.85$

Summary: Properties of water and their importance



Property	Comparison	Importance
Heat capacity (Cp; cal g^{-1} $°C^{-1}$) Thermal energy to raise 1 gm of a substance by 1 °C.	Highest of all solids & liquids, except liquid NH_3	Prevents extreme ranges in temperature; Energy transfer by water movements is large
Heat of fusion ($\Delta H = 79$ cal g^{-1}) Energy needed to break the hydrogen bonds.	Highest except for NH_3	Absorption or release of latent heat results in large thermostatic effects. Important for energy transfer and climate.
Heat of vaporization ($\Delta H = 540$ cal g^{-1}) Energy needed to convert water to vapor	Highest of all liquids	Thermostatic effect; Energy transfer
Boiling point (100 °C; projected -68°C) Freezing point (0 °C; projected -90 °C)	Much higher than expected (compared to other hydrides)	Water exists in 3 phases within the critical temperature range that accommodates life
Heat of freezing; only 1/7 that of evaporation	Low; Water structure can move easily into ice.	Implying relatively small difference in the # of bonds between water and ice
Surface tension; water likes itself relative to most other surfaces (7.2×10^{9} N m^{-1}) Measure of the strength of a liquid surface	Highest of all substances	Waves, drops and aerosol sea salt formation. Cell physiology
Dielectric constant; Charge insulation and dissolving power as a result of ion hydration (87 at 0 °C, 80 at 20 °C)	Highest of all substances except H_2O_2 and HCN	Solubility of salts & ion reactions
Dissolving power	Highest of all liquids both # of substances and quantities	Implications for biological and physical phenomena
Electrolytic dissociation	Very small	A neutral substance, yet contains both H^+ and OH^- ions
Transparency Absorption of radiant energy is large in IR and UV; Relatively uniform in the visible.	Relatively large	Water is "colorless"; Important for photosynthetic and photochemical reactions
Conduction of heat (a molecular process)	Highest of all liquids	Important for small-scale heat transfer, as in living cells.
Molecular viscosity ($= 10^{-3}$ N s m^{-2}) Measure of resistance to distortion (flow)	Less than most other liquids at same temperature.	Water flows readily to equalize pressure differences.
Compressibility	Relatively low (more similar to a solid)	Large increase in presses with depth causes only slight increase in density
Thermal expansion (for pure water it is at 4 °C)	Temperature of maximum density decreases with increasing salinity.	Waters with salinity less than 25 have maximum density at tempemperatures above the freezing point

Take home messages

- Physico-chemical properties of water determine its role in the environment
- Density anomaly regulates seasonality in temperate lakes
- Water acts as a climate regulator due to high heat capacity and heat of vaporation
- Presence of salt as a prerequisite for deep ocean convection
- Speciation in water depends on chemical environment, e.g. solution pH