Properties of Water

(Kalff Chapter 3, pp35-40)

The physical and chemical characteristics of water determine the physical and chemical characteristics of lakes, including density stratification, ice formation, and relatively stable temperature.

A. "Anomalous" properties of water (see Table 3-1, p 36, Kalff)

Water may be said to be an unusual substance. It has:

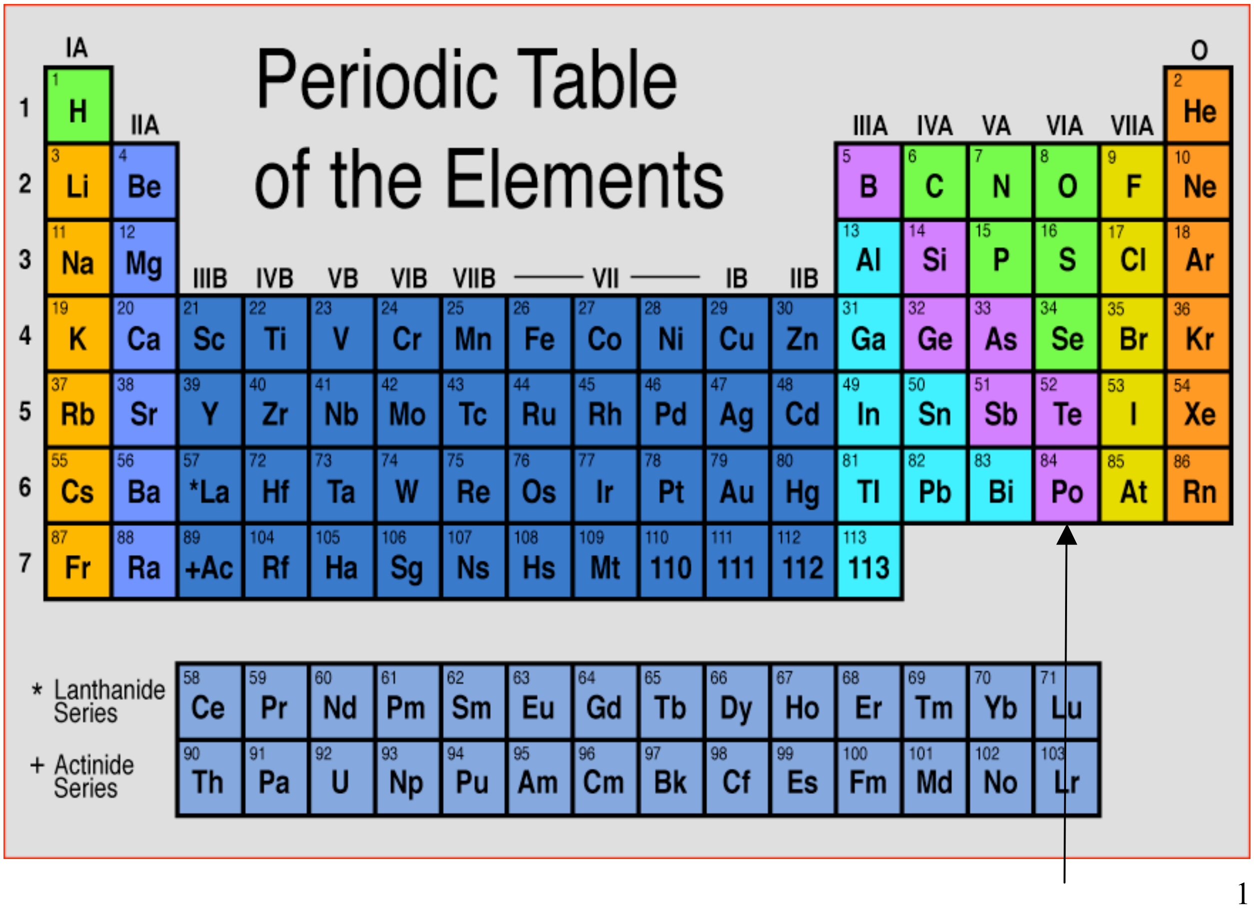
--the greatest heat capacity of any compound except ammonia

--the greatest surface tension, except mercury

--is the closest thing to a universal solvent

--has a melting point and a freezing point which are "too high"

For example, comparing melting point and boiling point of water with related compounds:



Periodic Table of the Elements

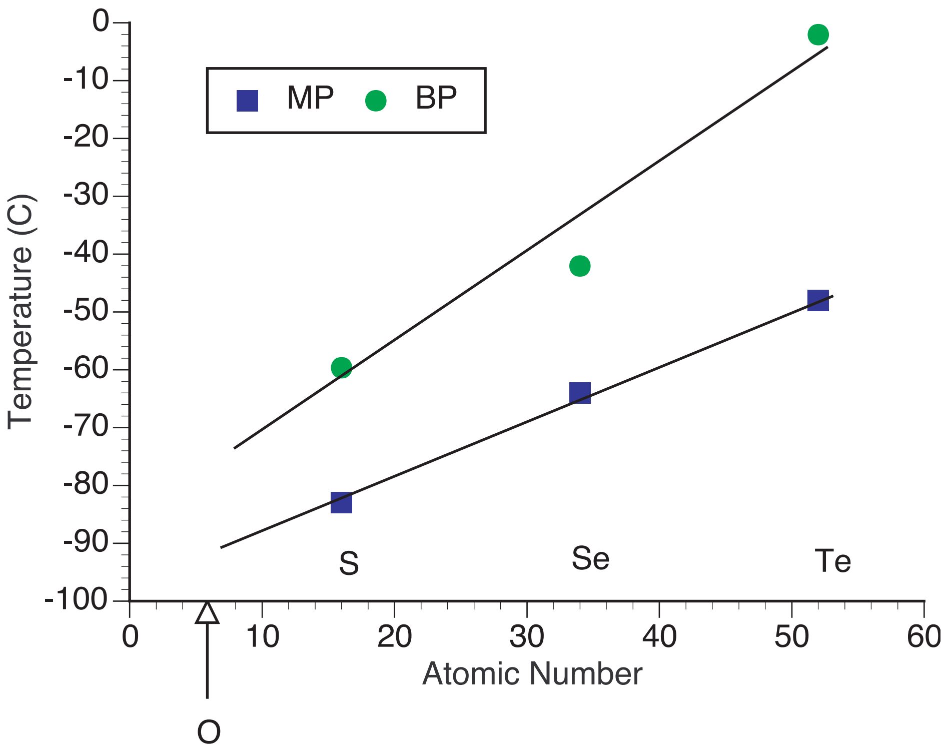
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII	VII	VII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	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
6	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
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 110	111 111	112 112	113 113					

* Lanthanide Series	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
+ Actinide Series	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

Element	Atomic Number	Atomic Mass	Compound	Melting Point	Boiling Point
Te Tellurium	52	127.61	H_2Te	-48	-2
Se Selenium	34	78.96	H_2Se	-64	-42
S Sulfer	16	32.01	H_2S	-82.9	-59.6
O Oxygen	8	16	H_2O	0	100

Source: Hutchinson (1957) p203.

Extrapolation from data on compounds of H with elements in the same column of the periodic table as O would predict a melting point of about -95 and a boiling point of about -75.



It is the structure of the water molecule which explains these properties of water. A water molecule may be described as consisting of an atom of oxygen to which are bound two atoms of hydrogen, the two atoms of hydrogen at an angle of 104.5 degrees from each other (i.e. **not** 180 degrees) and at a distance of 0.96 angstroms from the oxygen atom. The resulting molecule is asymmetric, and results in an electric dipole, causing one end of the molecule to possess a net negative charge (the oxygen end) and the other end a net positive charge. As a consequence of this dipole, adjacent molecules of water may be weakly bound together, via hydrogen bonds, giving liquid water a *three-dimensional structure*, particularly at low temperatures.

B. The structure of water (After J.L.Kavanau, "Water and Solute Water Interactions", 1964 QD 169 W3K3)

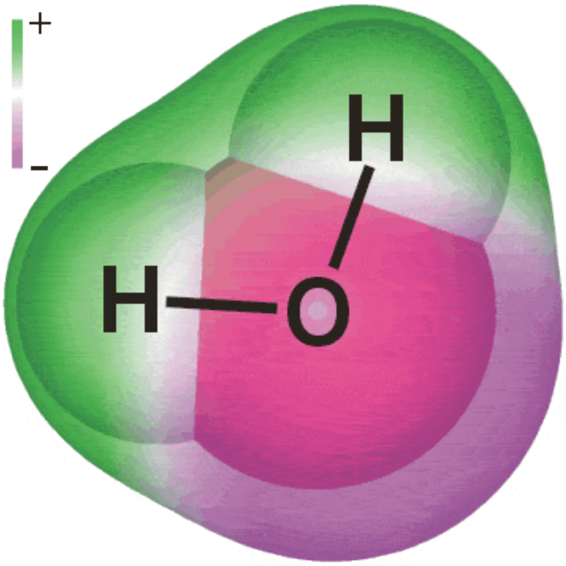
1. Water molecule (see figure 3-1, p37 of Kalff)

The basic cause of the anomalous properties of water stem from its basic structure:

dipole: The two H+ atoms are positively charged and the O atom is negatively charged. The strong electric dipole moment results from the asymmetric structure with displacement of charge. [The dipole moment is the product of the charge times the distance from the charge centers.] Water has a large electric dipole because of its geometry. [It acts].." as if the oxygen had two weak unsatisfied valencies, induced by the unshared pairs of electrons in the structural formulas just given: the hydrogens, owing to their capacity to form hydrogen bonds with sufficiently small electronegative atoms such as oxygen atoms, will act as if they had weak unsatisfied single valencies. This permits the association of the H_2O molecules in liquid water, a phenomenon which underlies practically all the anomalous properties of that remarkable substance."

Hutchinson, vol I, p196

This makes a water molecule polar, in that the oxygen end of the molecule has more electrons (a negative charge), while the hydrogen end has a slightly more positive end (as the electrons are found there less frequently). Having both a positive and negative end, water thus acts like an electromagnet. The positive end is able to attract negative ions or the negative end of other polar molecules. The negative end is able to attract positive ions or the positive end of other polar molecules. Because water does this very well, it is able to dissolve many substances, and it is thus called a universal solvent.



A water molecule

Shape and charge distribution on water molecule. The greater density of electrons on the O atom makes the molecule polar and allows H-bonding between molecules

2. Ice

Ordinary ice (ice I) (See figure 3-1, p37, Kalff)

"...ice has a highly open structure similar to the hexagonal form of silica (SiO_2) known as tridymite. Water molecules retain their individuality but participate in four hydrogen bonds. Each oxygen atom is surrounded tetrahedrally at a distance of 2.76 Angstroms by the four other oxygen atoms to which it is hydrogen bonded. The hydrogen atoms, however, are distributed asymmetrically, lying on lines connecting adjacent hydrogen-bonded oxygen atoms but closer to one oxygen atom than to the other. Each oxygen atom has two hydrogen atoms near it (the two hydrogen atoms of the molecule) at an estimated distance of about 0.96 to 1.02 angstroms, linked to it by strong bonds, and two further away (the hydrogen atoms of the two neighboring molecules) at an estimated distance of about 1.74 to 1.80 angstroms..."

There several other forms of ice--ice II, III, IV, V, VI, VII, VIII, Ic, and "vitreous ice".

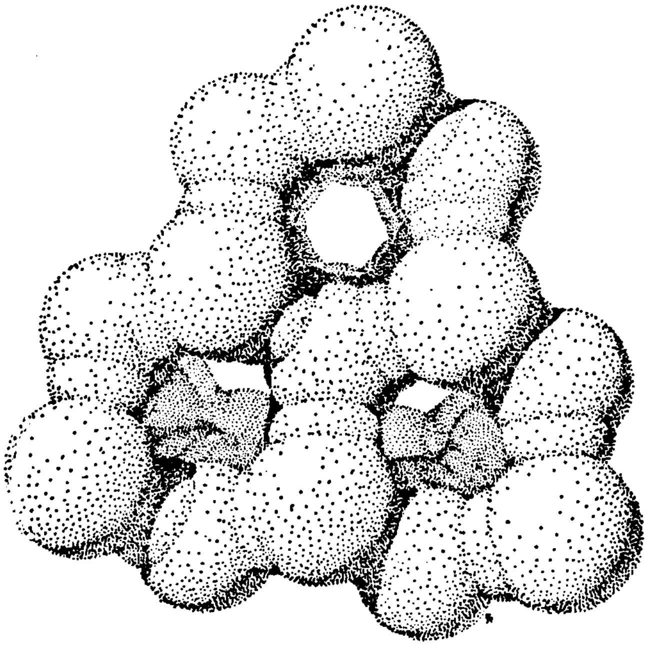


FIGURE 2-2 A diagrammatic representation of an ice crystal showing the van der Waals radii of the atoms and open voids between the aggregated molecules. (From Pimental, G. C., and McClellan, A. L.: *The Hydrogen Bond.* San Francisco, W. H. Freeman and Co., copyright © 1960.)

3. Structure of liquid water

Kalff, p35: "Liquid water is a liquid crystal rather than a true fluid."

According to Kavanaug: "The distinctive structural features of liquid water generally have been ascribed to its partial retention of the tetrahedrally directed hydrogen-bonding involved in the crystalline structure of ice--i.e., as a broken-down form of the ice lattice--but with the length of the O...H...O bond increased. Not only are the orientations of the water molecules far from random, but the molecules oscillate torsionally with rather small amplitudes instead of rotating freely....X-ray scattering studies indicate that the average number of nearest neighbors is 4.4 to 4.6 (probably fluctuating between 4 and 6) and that the average distance between centers is 2.92 angstroms. A high concentration of molecules is found at 4.75 to 4.90 angstroms, which is roughly the expected distance for the next-nearest neighbors if the molecules tend to have a tetrahedral arrangement as in ice...Water can be regarded as a particular type of associated liquid in which the association penetrates through the whole volume of the liquid, forming a three-dimensional network, several different configurations of which can coexist simultaneously. Each of the characteristic configurations corresponds to a characteristic free energy, to characteristic dielectric properties, to a characteristic molecular volume, etc. A change in temperature leads to a change in the relative numbers of molecules associated in each configuration, these shifts accounting for the anomalous properties of water. Most modern theories of water take as a starting point this view that water is a mixture of certain three-dimensional structures.." (Kavanaug, 1964)

4. Auto ionization (dissociation of a water molecule to form H^+ and OH^-)

Recent calculations (by Geissler et al., 2001) suggest that hydrogen bonds are also important to the process of auto ionization of water. They describe a process (based on calculations) involving the transfer of protons along a hydrogen bond "wire". If the nascent ions separate by 3 or more neighbors, followed by the bond wire connecting the two ions being broken, a metastable charged state is created. "The ions may then diffuse to large separations." Thus they postulate that the framework of hydrogen bonds among a chain of adjacent molecules of water provides a pathway for the formation of separated hydrogen and hydroxyl ions. Once again, the appeal is to the structure of liquid water via hydrogen bond chains. An interesting feature of their analysis is a particular prediction: that transient (100 femtosecond) populations of hydronium and hydroxide ions should exist in bulk water. This prediction may lead to empirical confirmation. "**The brave experimentalist who picks up the gauntlet and identifies the predicted transient species will write the next chapter of this story**." (same issue of Science, p2107) Reference: Geissler et al. 2001. "Auto-inonization in Liquid Water". Science 291:2121-2124. (March 16 issue)

The point? : *there is more to be learned about water!*

C. Physical properties of water of interest to Limnology

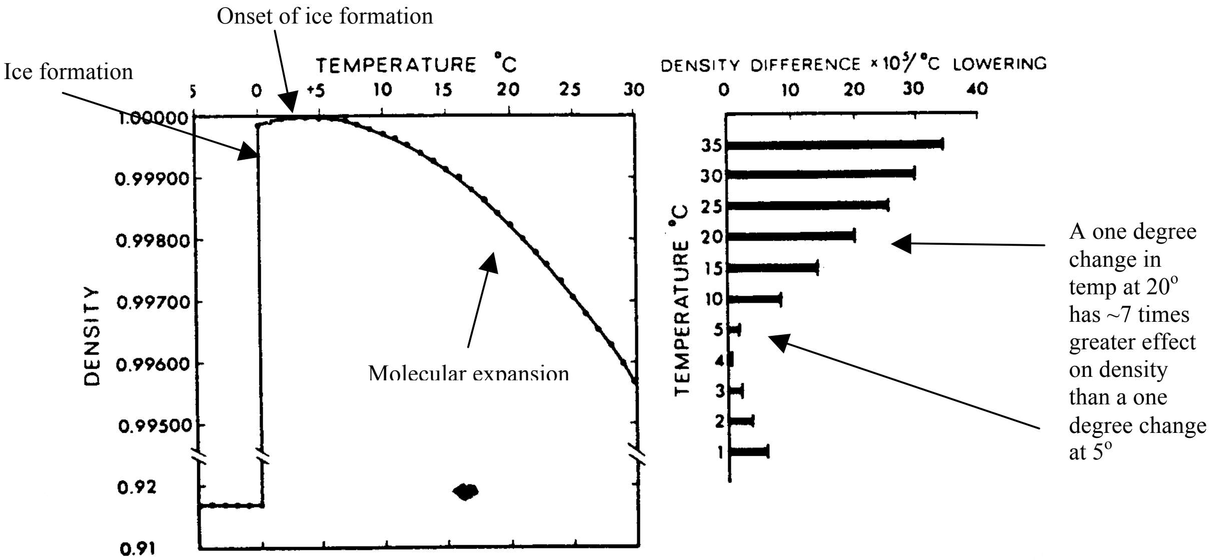
1. **Density**

The high density of water and the effects of temperature and salinity on density determine most chemical and biological characteristics of lakes. The high density of water (775 times greater than air at standard temperature and pressure (0 C and 760 mm Hg)) makes aquatic organisms buoyant against gravitational pull and reduce the energy needed to for support. This is most evident in aquatic vascular plants.

a. Effect of temperature

The density of water is a function of the temperature. The density of water first increases, from 0 to 3.98 degrees C, and then begins to decrease. Thus, the temperature of maximum density of pure water is 3.98 degrees C. This initial increase in density with increasing temperature is presumed t result from the decreasing significance of the ice-like form of water, with its open lattice and therefore lower density, and to increasing significance of a more compact form of water, perhaps a "ball-pack of greatest density".

Also, as temperature increases away from 3.98 the density difference per degree change in temperature increases (see figure 3-2, p37, Kalff). For example, a temperature change from 4 to 5 degrees C has a much smaller impact on density than a change from 35 to 36 degrees.



Onset of ice formation

Ice formation

Molecular expansion

A one degree change in temp at 20° has ~7 times greater effect on density than a one degree change at 5°

FIGURE 2-3 Density (g ml^{-1}) as a function of temperature for distilled water at 1 atm. The density difference per °C lowering is shown in the right-hand portion of the figure at various temperatures. (Modified from Vallentyne, 1957.)

b. Effects of salinity

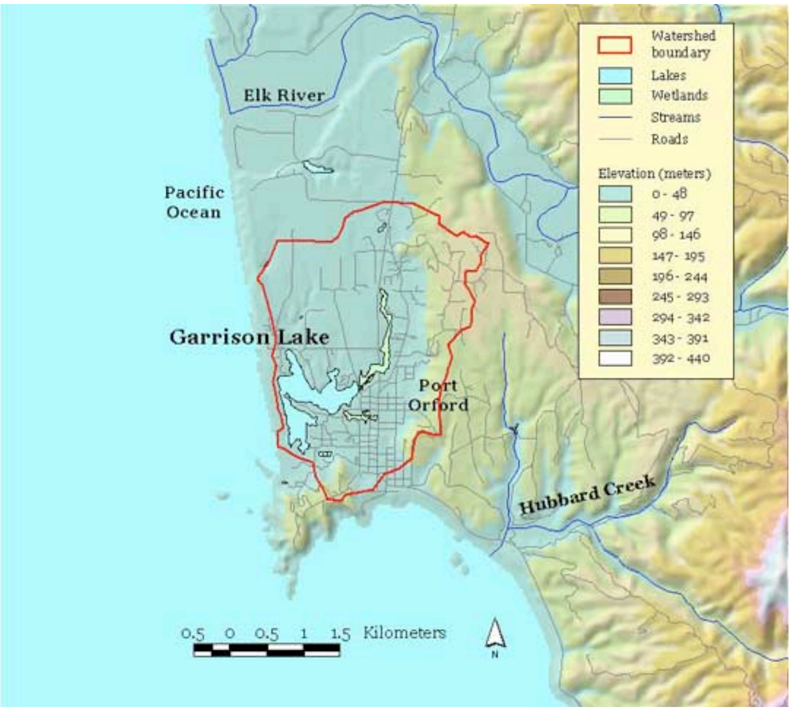
Density is increased by increasing salinity.

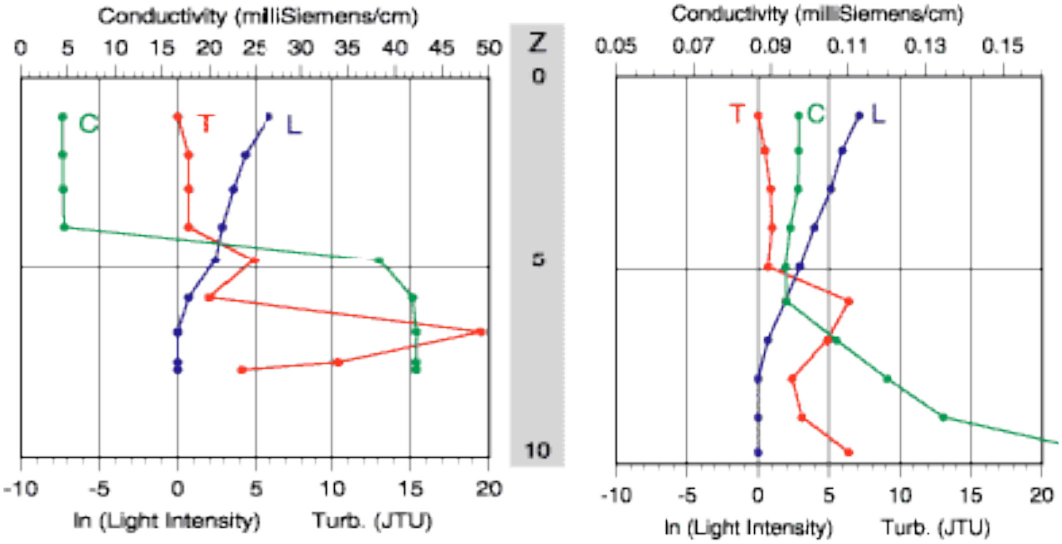
Salt content	Density at 4 degrees
0	1.00000
1 ppt	1.00085
2 ppt	1.00169
3 ppt	1.00251
10 ppt	1.00818
35 ppt	1.02822

(assuming sea water ion ratios)

The effect may seem small, but consider for example a lake 100M x 100M x 2M deep composed of a bottom layer of seawater (1 M) and a surface layer of fresh water. The bottom layer will exceed the mass of the surface layer by 282 metric tons. (a metric ton = 1000 kg)

Note example of Garrison Lake. Garrison Lake periodically is inundated by seawater during storms. The seawater settles in the bottom of the lake, setting up a density gradient. A lake that is exhibits permanent density stratification caused by salinity is termed **meromictic**. Compare the conductance (a measure of salinity) of Garrison Lake and Bradley Lake. Bradley Lake is located north of Garrison Lake in a similar geologic and climate, but does not experience saltwater intrusion. A new outlet was constructed that stabilized the lake level and in the winter of 2008/9 the salt water layer at the bottom of the lake disappeared.





Garrison Lake and Bradley Lake

profiles on 7/20/01 (T= turbidity, C=conductance, L=light

Note that the effect of salinity can be much stronger than the effect of temperature. For example, the density of pure water at 21 degrees C is about 0.998 vs. 1.000 at 4 degrees C, or about 2 parts per 1000 difference. By contrast (see table above) seawater is about 28 parts per thousand denser than freshwater. The seemingly small difference can have a profound effect on the permanence of stratification.

c. Other factors

Other factors (pressure, isotopic content, suspended sediment) may also influence density.

Important consequences of the density characteristics of water are the annual cycle of stratification and the significance of buoyancy for aquatic organisms.

2. Viscosity (See table 3-2, p39, Kalff)

An object moving through a fluid experiences frictional resistance. This property of the fluid is described as **dynamic viscosity**. The resistance to movement is proportional to:

-the surface area of the falling body

-the speed of movement

-a constant, which is a property of the fluid in question, and is expressed as the "coefficient of viscosity".

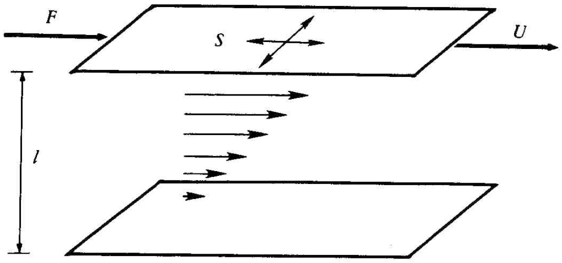
Thus: $\tau = \mu \, du/dz$, where:

du/dz is the velocity change in the water perpendicular to the direction of motion,

μ is the viscosity coefficient, with dimensions of g/cm sec,

$$\mu = Fl/US$$

τ is the frictional stress, per unit area, between adjacent layers, and has the units of dynes/cm^2 (force/area).



An ideal pair of thin, flat plates. If the lower plate is fixed, it takes a force to keep the upper one moving. The magnitude of that force is proportional to the dynamic viscosity of the fluid between them. The length of each horizontal arrow between the plates is proportional to the local flow speed.

The coefficient μ is a function of temperature:

Temperature	0	10	20	30	40
Coefficient (g/cm-sec)	0.018	0.0131	0.0100	0.0080	0.0065

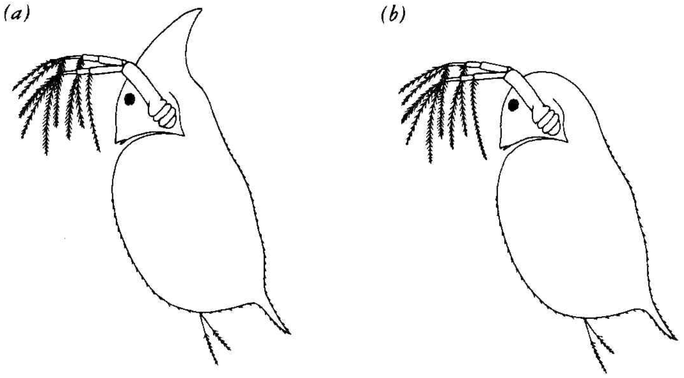
Viscosity at 0 C is nearly 2x that at 20 C!

Viscosity is of tremendously significance the plankton. In effect, it is the viscosity of the water that makes the existence of plankton possible.

Viscosity of water offers approximately 100x more frictional resistance to a moving organism or particle than air. Organisms in locomotion must expend considerable energy to overcome resistance due to viscosity.

Change in viscosity with temperature has been proposed as one explanation for cyclomorphosis in daphnia, a microcrustacean. Lower viscocity at higher temperatures result in high sinking rates. As a consequence, more swimming power is needed to maintain position in the water column. The larger head on the warm water forms (see below) allow attachment of larger muscles for moving the second antennae, the primary propulsive organ, and permit a great stroke amplitude. Evidence is circumstantial and not conclusive (S.Vogel "*Life in Moving Fluids*") and there are other theories about the cause of cyclomorphisis in the plankton that we will discuss later.

The cladoceran water flea, *Daphnia*, (*a*) in warm water form, and (*b*) in cold water form.



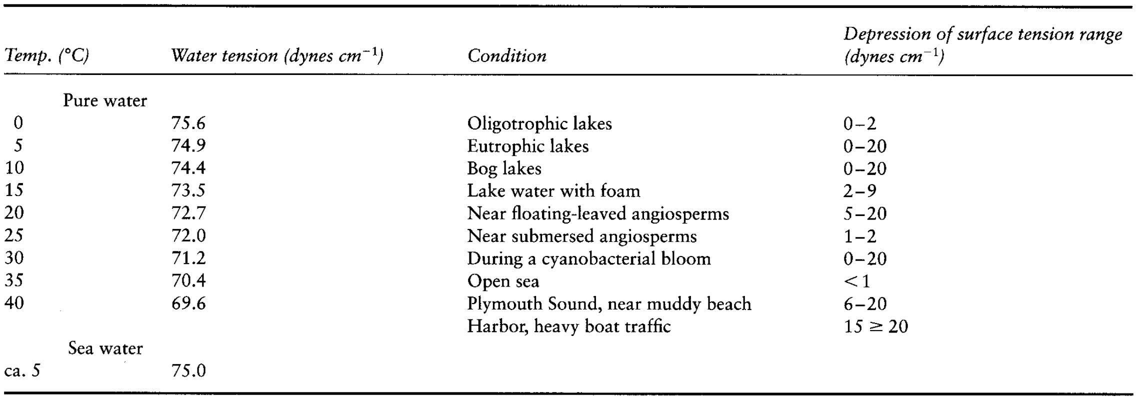
Kinematic viscosity = dynamic viscosity/density. This term is used to calculate the "gooiness" of a fluid – how easily it flows, how likely it is to break into vortices.

3. Surface tension

A molecule near the surface is subjected to a resultant force directed back into the liquid (because of the imbalance of alternative forces between molecules). A molecule at the surface can be considered as having a potential energy greater than that of a molecule in the interior by the work that has been done against this force in bringing the molecule from the interior of the liquid to the surface. A liquid thus has a surface potential energy proportional to its surface area.

Water has the highest surface tension (73.5 dynes @ 15 degrees) of any liquid save mercury. Surface tension is lowered by increasing temperature and increased inorganic salts.

TABLE 2-2 Surface Tension of Water with Changes in Temperature and Its Depression in Natural Waters under Various Conditions



Temp. (°C)	*Water tension (dynes cm^{-1})*	*Condition*	*Depression of surface tension range (dynes cm^{-1})*
Pure water			
0	75.6	Oligotrophic lakes	0–2
5	74.9	Eutrophic lakes	0–20
10	74.4	Bog lakes	0–20
15	73.5	Lake water with foam	2–9
20	72.7	Near floating-leaved angiosperms	5–20
25	72.0	Near submersed angiosperms	1–2
30	71.2	During a cyanobacterial bloom	0–20
35	70.4	Open sea	<1
40	69.6	Plymouth Sound, near muddy beach	6–20
		Harbor, heavy boat traffic	$15 \geq 20$
Sea water			
ca. 5	75.0		

From data of Adam (1937), Hardman (1941), and Goldacre (1949).

There is a unique community of organisms, termed the **neuston**, associated with the surface film, and using the surface tension as an anchor. Surface tension can support some relatively large organisms, such as water striders (Gerridae) and other beetles, but can be a trap for others. Microcrustacea that are caught at the interface between air and water by wave action can become trapped and cannot reenter their normal submersed habitat.

4. Specific heat, heats of fusion and evaporation.

The specific heat of a substance is the amount of heat required to increase a gram of the substance by 1 degree Celsius [To be completely precise, it is necessary to specify c_p, specific heat at constant pressure, or c_v, specific heat at constant volume]. For water, c=1. (A consequence of how metric units were defined.)

Latent heat of evaporation

The heat absorbed by water on evaporation at the boiling point is 539.6 calories/gram.

Latent heat of fusion

The heat required to convert 1 gram of ice to 1 gram of liquid water, at 0 degrees, is 79.7 calories/gram.

These thermal properties of water give a large body of water a considerably degree of "**thermal inertia**". Water temperature changes slowly. The thermal characteristics of water also influence the local climate. Michigan, for example, has milder winter temperatures than continental areas due to the thermal capacity of the Great Lakes. Those of us on the west side of the Cascades also benefit from the thermal capacity of the Pacific Ocean, which moderates our winter and summer temperatures relative to Eastern Oregon.

5. Colligative properties

The colligative properties are unique properties of solutions, and are a function of the number of dissolved ions.

vapor pressure lowering

freezing point depression

boiling point elevation

osmotic pressure

A consequence of osmotic pressure:

Salt water fish tend to lose water to the ambient seawater, and must therefore drink seawater and excrete ions to maintain water balance. Freshwater fish absorb water from their more dilute surroundings and must secrete hypotonic urine to avoid bloating.

6. Relative permittivity or dielectric constant

The relative static permittivity of a solvent is a relative measure of its polarity. For example, water (very polar) has a dielectric constant of 80.10 at 20 °C while n-hexane (very non-polar) has a dielectric constant of 1.89 at 20 °C. A vacuum has a permittivity of 1 by definition. This information is of great value when designing separation, sample preparation and chromatography techniques in analytical chemistry.

The dielectric constant of water is 80, meaning that two opposite charges in water attract each other with a force only 1/80th as strong as in air. As a consequence of its high dielectric constant, water is an efficient solvent for ions (salts).