Università degli studi di MILANO
Facoltà di AGRARIA

El. di Chimica e Chimica Fisica
Mod. 2 CHIMICA FISICA

Lezione

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Anno Accademico 20010-2011

Only about 3% of Earth's water is fresh. Two percent of the Earth's water (about 66% of all fresh water) is in solid form, found in ice caps and glaciers.

Because it is frozen and so far away, the fresh water in ice caps is not available for use by people or plants.

That leaves about 1% of all the Earth's water in a form useable to humans and land animals.

This fresh water is found in lakes, rivers, streams, ponds, and in the ground. (A small amount of water is found as vapor in the atmosphere.)

L'acqua è la componente principale del corpo umano, rappresenta un nutriente essenziale.

L’acqua totale corporea (ATC) costituisce l’80% del peso nel bambino, il 70% nell’adulto, mentre scende al 60% nell’anziano.

Le funzioni metaboliche

L’acqua ha molteplici funzioni metaboliche, in particolare:

Trasporto di sostanze nutritive

Partecipazione alle reazioni metaboliche

Partecipazione alla regolazione della temperatura corporea

Regola il volume corporeo, ed il flusso delle scorie metaboliche.

La molecola

Lewis Dot Structures: Lewis dot structures are a shorthand to represent the valence electrons of an atom. The structures are written as the element symbol surrounded by dots that represent the valence electrons. The Lewis structures for the elements in the first two periods of the Periodic Table are shown below.

H•	**Lewis Dot Structures**							He:
Li•	Be		B	C	N	O	F	Ne

Polar and Non-Polar Covalent Bonding

There are, in fact, two sub-types of covalent bonds. The H_2 molecule is a good example of the first type of covalent bond, the non-polar bond. Because both atoms in the H_2 molecule have an equal attraction (or affinity) for electrons, the bonding electrons are equally shared by the two atoms, and a non-polar covalent bond is formed. Whenever two atoms of the same element bond together, a non-polar bond is formed.

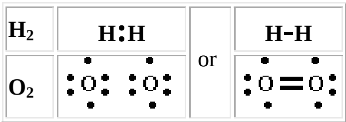


table 3–2

The Electronegativities of Some Elements	
Element	**Electronegativity***
F	4.0
O	3.5
Cl	3.0
N	3.0
Br	2.8
S	2.5
C	2.5
I	2.5
Se	2.4
P	2.1
H	2.1
Cu	1.9
Fe	1.8
Co	1.8
Ni	1.8
Mo	1.8
Zn	1.6
Mn	1.5
Mg	1.2
Ca	1.0
Li	1.0
Na	0.9
K	0.8

*The higher the number, the more electronegative (the greater the electron affinity of) the element.

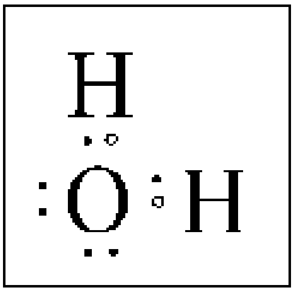
Molecular dipoles are the result of covalent bond formation between atoms of different electronegativity. Electronegativity is a property of atoms within molecules and quantifies the relative attraction of shared electrons in covalent bonds for an atom.

Cox, Lehninger Principles in Biochemistry, chapter 3

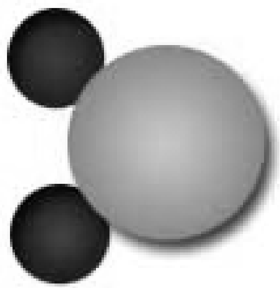
Elettronegativita'

Tendenza di un atomo ad attrarre gli elettroni di un legame. E' definita come la media aritmetica tra il potenziale di ionizzazione e l'affinità elettronica. I valori riportati sono valutati su una scala relativa che ha come riferimento il Fluoro la cui elettronegatività e posta convenzionalmente uguale a 4.0.

A polar bond is formed when electrons are unequally shared between two atoms. Polar covalent bonding occurs because one atom has a stronger affinity for electrons than the other (yet not enough to pull the electrons away completely and form an ion). In a polar covalent bond, the bonding electrons will spend a greater amount of time around the atom that has the stronger affinity for electrons. A good example of a polar covalent bond is the hydrogen-oxygen bond in the water molecule.

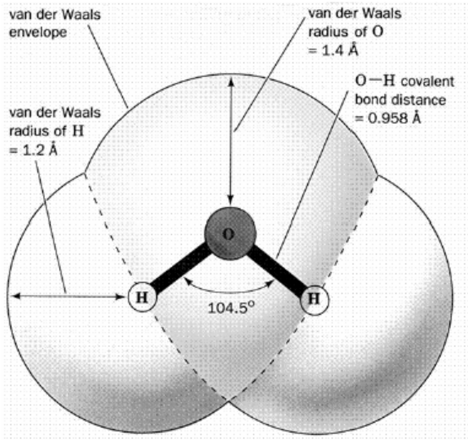


Water molecules contain two hydrogen atoms (pictured in red) bonded to one oxygen atom (blue). Oxygen, with 6 valence electrons, needs two additional electrons to complete its valence shell. Each hydrogen contains one electron. Thus oxygen shares the electrons from two hydrogen atoms to complete its own valence shell, and in return shares two of its own electrons with each hydrogen, completing the H valence shells.



H_2O : a water molecule

Life … it's all about the water molecule

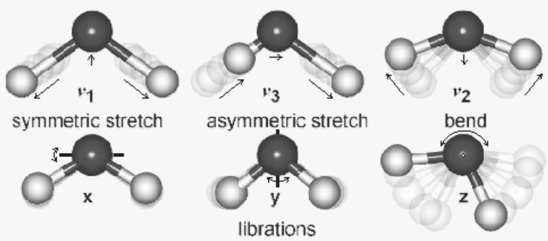


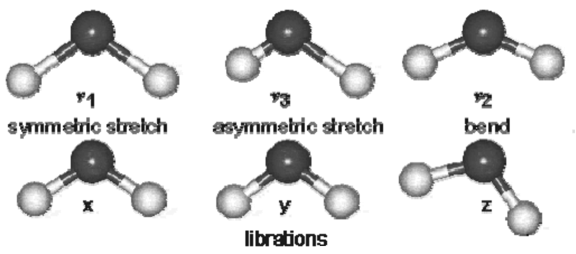
Voet and Voet, Biochemistry, 1995, 2nd ed, chapter 2, figure 1

Water vapor spectroscopy has been recently reviewed [348]. The water molecule may vibrate in a number of ways. In the gas state, the vibrations [607] involve combinations of symmetric stretch (v_1), asymmetric stretch (v_3) and bending (v_2) of the covalent bonds with absorption intensity ($H_2{}^{16}O$) v_1;v_2;v_3 = 0.07;1.47;1.00 [8]. The stretch vibrations of $HD^{16}O$ refer to the single bond vibrations, not the combined movements of both bonds.

	v_1, cm^{-1}	v_2, cm^{-1}	v_3, cm^{-1}
$H_2{}^{16}O$	3657.05	1594.75	3755.93
$H_2{}^{17}O$	3653.15	1591.32	3748.32
$H_2{}^{18}O$	3649.69	1588.26	3741.57
$HD^{16}O$	2723.68	1403.48	3707.47
$D_2{}^{16}O$	2669.40	1178.38	2787.92
$T_2{}^{16}O$	2233.9	995.37	2366.61

Shown opposite are the main vibrations occurring in water. The movements are animated using the cursor. The dipole moments change in the direction of the movement of the oxygen atoms as shown by the arrows.





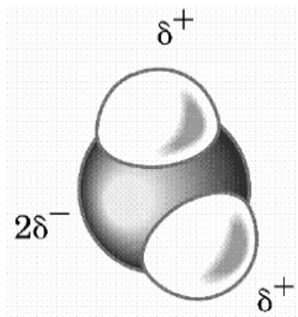
… and asymmetries in electron distributions.

Dipole moment ($\delta^+ \rightarrow \delta^-$)

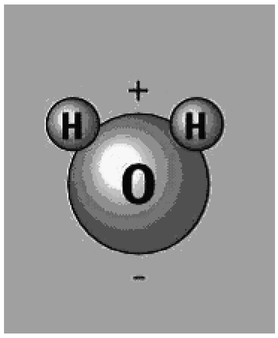
$\mu = Q\,r$

$\mu(H_2O) = 1.85$ Debye

1 Debye = 3.33×10^{-30} Cm

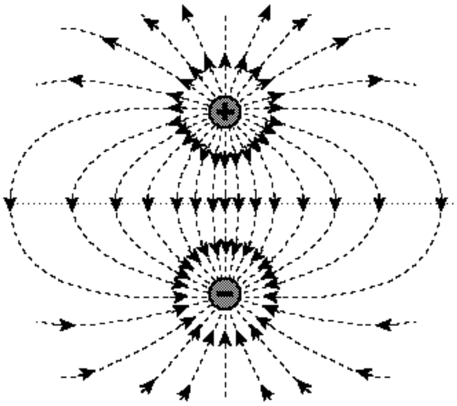


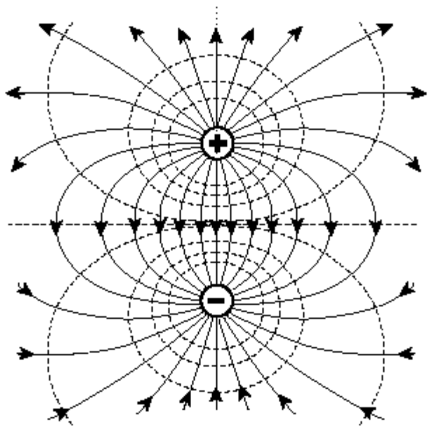
Cox, Lehninger Principles in Biochemistry, chapter 4, figure 1



Direction of electric dipole

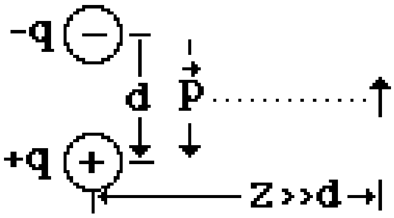
$\vec{p}=q\vec{d}$



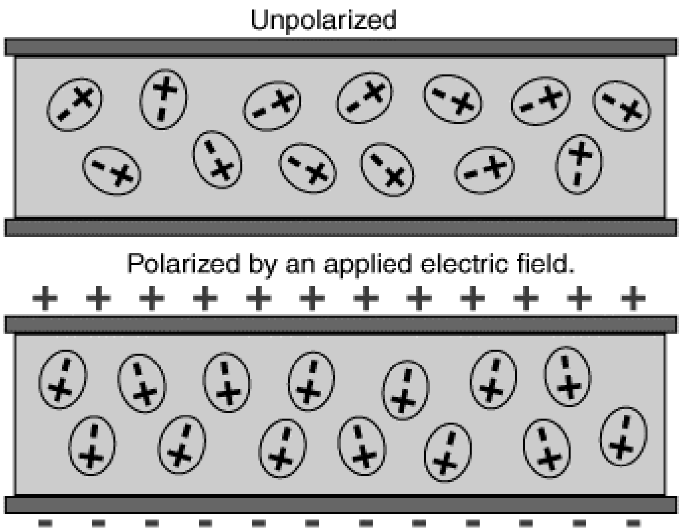


Equipotential lines: dipole

The electric potential of a dipole show mirror symmetry about the center point of the dipole. They are everywhere perpendicular to the electric field lines.



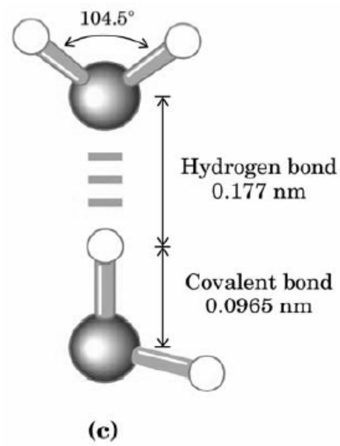
$$E = \frac{1}{4\pi\varepsilon_0}\frac{p}{z^3}$$



- Costante dielettrica relativa a 25 °C = 78,5

O – H bond distances:

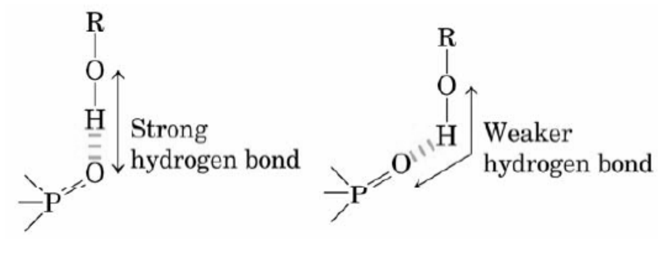
1Å = 0.1nm = 10^{-10}m



Cox, Lehninger Principles in Biochemistry, chapter 4, figure 1

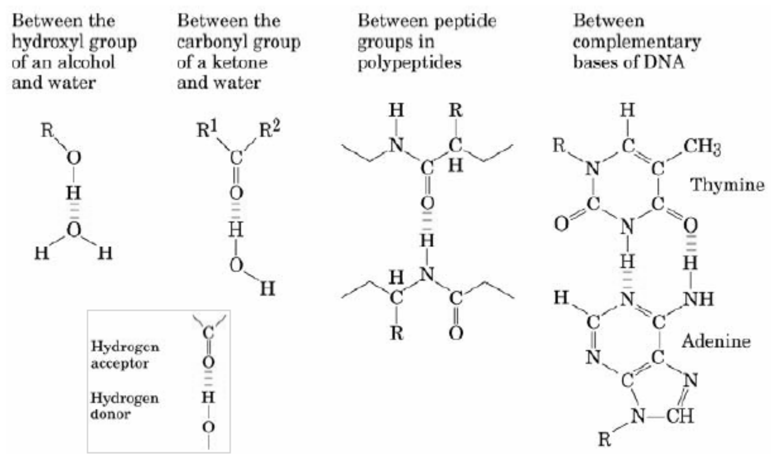
Hydrogen bonds are linear structures.

Hydrogen bonds stabilize molecular interactions of select orientation.



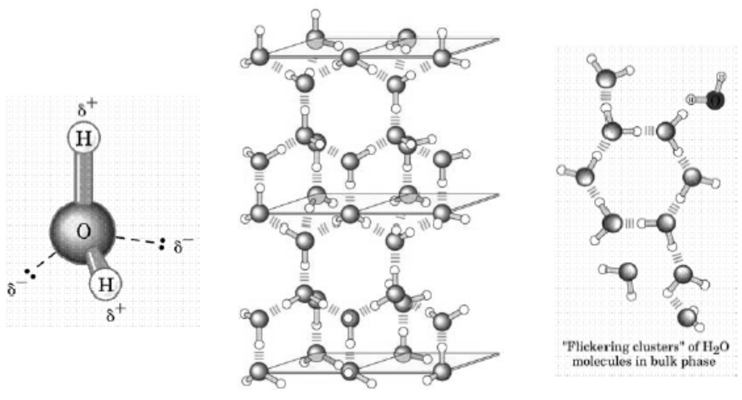
Cox, Lehninger Principles in Biochemistry, chapter 4, figure 5

Important hydrogen bonds in biological molecules



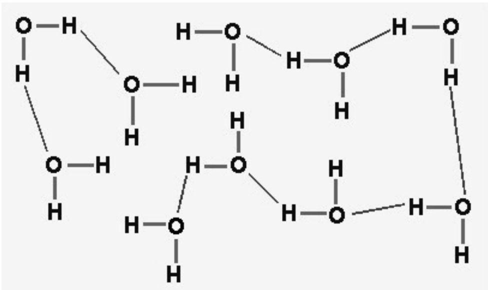
Cox, Lehninger Principles in Biochemistry, chapter 4, figure 4

The crystal structure of ice demonstrates the tetrahedral dipole structure of water molecules. In liquid water, less then 3 hydrogen bonds are formed per water molecule at any given time.



Solid Liquid

Cox, Lehninger Principles in Biochemistry, chapter 4, figure 1, 2



Rappresentazione schematica planare di molecole di acqua con legami di idrogeno.
Nel disegno i legami OH di ogni molecola appaiono, per semplicità, disegnati a 90° tra loro (sappiamo che non è vero!); in verde i legami covalenti normali; in rosso i legami a idrogeno.
Quanto più questi ultimi sono lunghi, tanto più essi sono allentati, perciò o si stanno formando o si stanno rompendo.
Quando un legame di idrogeno si forma, si possono allentare quelli covalenti preesistenti, che si possono rompere a loro volta, in una situazione di totale dinamicità.

Water is stable.

Entalpia standard di formazione a 25°C

Mr 18.02 $H_20(g)$: -241.82 kJ mol^{-1}

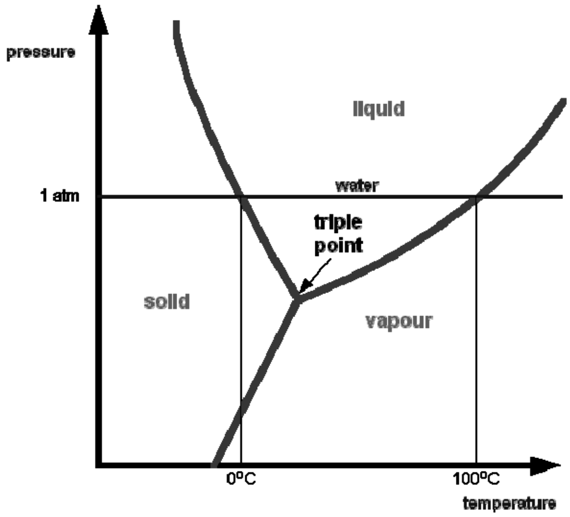
Mr 34.080 $H_2S(g)$: -20.6 kJ mol^{-1}

Mr 17.031 $NH_3(g)$ -46.11 kJ mol^{-1}

It is stable at very high temperatures.

Water is relatively stable chemically. It ionises only slightly, but will hydrolyse or react with a number of materials. Many reactions are catalysed by the addition of very small amounts of water, with corrosion being an outstanding example.

Water is the only substance on Earth that exists in all three **physical states of matter**: **solid**, **liquid**, and **gas**.



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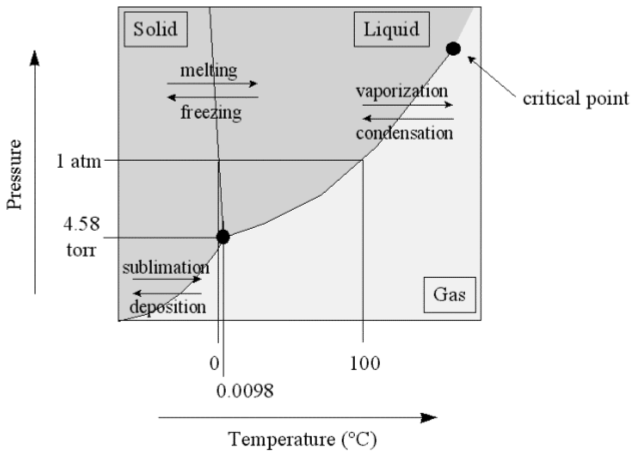


$p_c \approx 22$ Mpa,

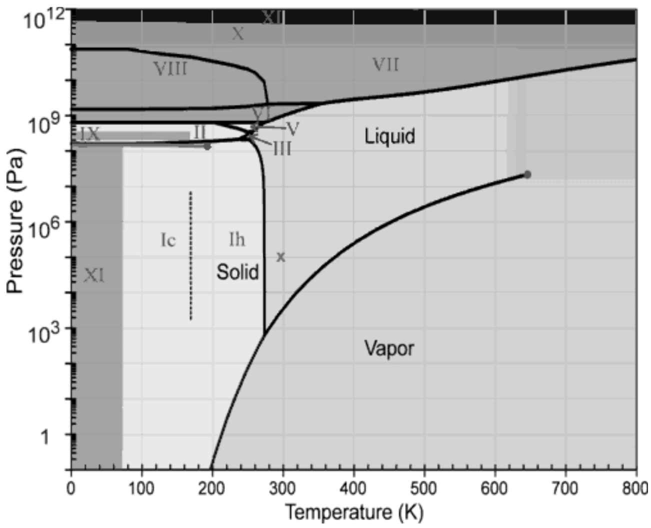
$T_c \approx 647$ K

Water has a relatively high boiling point (100°C) at 760mm Hg).

Triple point 0.01C and 611.73 Pa (4.589 mm Hg)

Temperatura (°C)	Pressione del vapore saturo dell'acqua (mmHg)	Temperatura (°C)	Pressione del vapore saturo dell'acqua (mmHg)
0	4,57	22	19,83
3	5,69	23	21,10
5	6,54	24	22,40
8	8,04	25	23,80
10	9,21	26	25,21
11	9,84	27	26,74
12	10,50	28	28,35
13	11,23	29	30,04
14	12,00	30	31,80
15	12,80	35	42,20
16	13,63	40	55,32
17	14,53	50	92,50
18	15,50	60	149,40
19	16,48	80	355,10
20	17,50	90	525,80
21	18,65	100	760,00

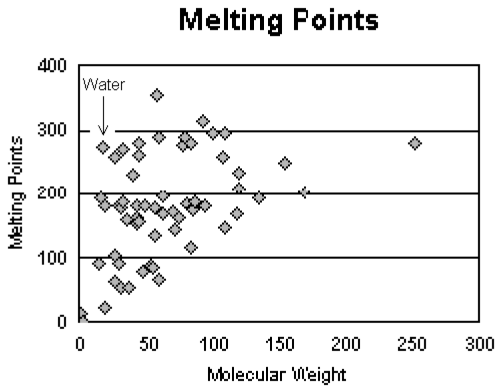
Water is the only substance on Earth that exists in all three **physical states of matter**: **solid**, **liquid**, and **gas**.



Water exists as a liquid over an important range of temperature from 0 - 100° Celsius. This range allows water to remain as a liquid in most places on the Earth.

Freezing Point of Water

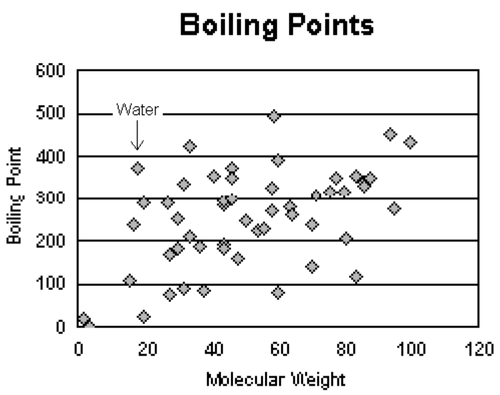
The next diagram below shows the melting temperature of a number of substances against their atomic or molecular weights. The scale is in Kelvins. The arrow near the top left points to the value for water, which has a high melting point for its molecular weight. If water were a more typical liquid we would seldom see ice.



Boiling point of water

The next diagram shows the boiling temperature, in Kelvins, of a number of substances against their atomic or molecular weights, under normal pressure.

Once again the value for water, shown by the arrow, is unexpectedly high. Since 300 K represents an average temperature in many places, it is clear that water would be vapourized under normal conditions if it had a more typical boiling temperature.



The water molecules in the liquid state are so strongly associated that a large amount of energy in the form of heat is needed to break loose a molecule into the gas state. As a result, the boiling point and heat of vaporisation of water are very high for this low molecular weight material

Entalpia di evaporazione	40.67 kJ mol^{-1}	(373 K)
	44.01 kJ mol^{-1}	(298 K)

Entalpia di fusione	6.009 kJ mol^{-1}	

Entalpia sublimazione	50.91 kJ mol^{-1}	(273.15 K)

Incorporated in the changes of state are massive amounts of heat exchange. This feature plays an important role in the redistribution of heat energy in the Earth's atmosphere. In terms of heat being transferred into the atmosphere, approximately 3/4's of this process is accomplished by the evaporation and condensation of water.

Water has a high specific heat. Because water has a high specific heat, it can absorb large amounts of heat energy before it begins to get hot. It also means that water releases heat energy slowly when situations cause it to cool. Water's high specific heat allows for the moderation of the Earth's climate and helps organisms regulate their body temperature more effectively.

Mari e grandi laghi, a causa dell’alta capacità termica dell’acqua, stabilizzano la temperatura dell’ambiente

<u>Calore specifico</u>: quantità di calore necessaria per fare aumentare di 1 °C la temperatura di una specifica massa di sostanza. Esso dipende dalla natura della sostanza, dalla temperatura e dalla pressione (da quest'ultima in particolare per i gas)

$$Cp = \left(\frac{\partial H}{\partial T}\right)_P$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$Cp \propto \text{gradi di libertà}$$

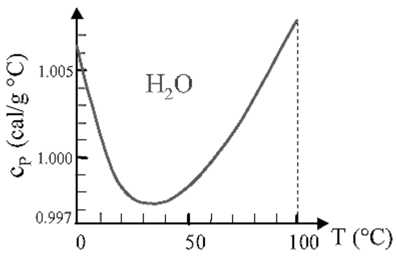
Il calore specifico dell'acqua, 1 Cal/g °C a 14.5 °C e 1 atm, è superiore a quello della maggior parte delle altre sostanze. In Fig. 1 è rappresentato il calore specifico dell'acqua nell'intervallo di temperature 0 °C - 100 °C. Si osservi la sua dipendenza dalla temperatura (la scala delle ordinate è molto amplificata!); mediamente il suo valore si attesti intorno a circa 1 cal/g °C.

1cal = 4.184 J

$Cp(s)=37\ J\ K^{-1}\ mol^{-1}$

$Cp(l)=75.291\ J\ K^{-1}\ mol^{-1}$ a 25°C

$Cp(g)=33.58\ J\ K^{-1}\ mol^{-1}$ a 25°C



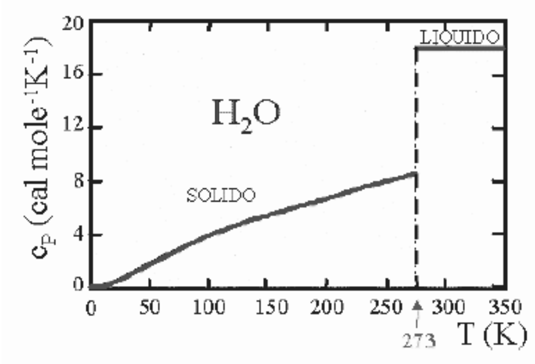
$Cp(g) = a + bT$

$a = 30.54\ J\ K^{-1}\ mol^{-1}$

$b = 10.29 \cdot 10^{-3}\ J\ K^{-2}\ mol^{-1}$

$Cp(l)=75.48\ J\ K^{-1}\ mol^{-1}$

Calore specifico a pressione costante, c_p, dell'acqua in funzione della temperatura



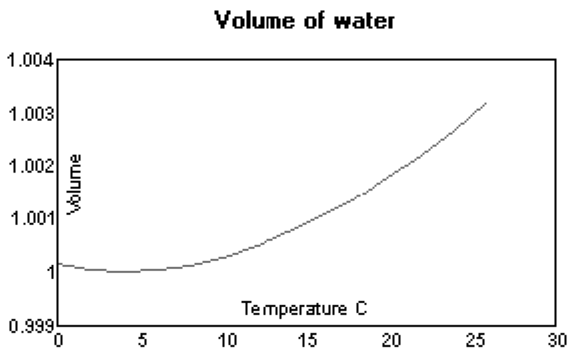
ΔCp fusione 37.3 J K^{-1} mol^{-1}

ΔCp vaporizzazione 41.9 J K^{-1} mol^{-1}

Density of Water

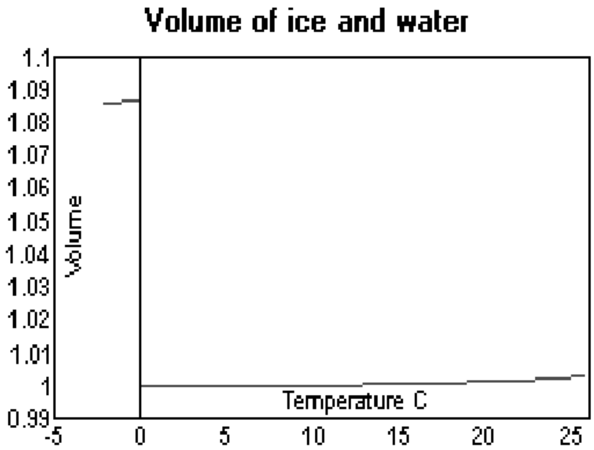
Most substances expand as the temperature is raised, and water does the same, except between its freezing point, 0 C, and 4 C. In that range, water expands when it cools, becoming less dense. This has interesting consequences. The first diagram below shows a graph of volume against temperature for a given mass of water.

In most cases the cooler liquid would tend to sink, allowing fresh liquid to reach the top and be cooled by the cold air. In the case of water, when it goes below 4 C, it will tend to float, so that cooling by convection is reduced, leaving conduction as the only mechanism. So the mass of water in a pond will cool more slowly as a result.



Density (g/cm3)	
0.99821	20 °C
0.9984	0 °C

Water expands when it freezes, as shown in the picture above, which has interesting consequences for water pipes in winter. It also means that ice floats on water, preventing convection from bringing more water into contact with the air. This tends to reduce the rate at which more water freezes. The consequences for life in the water are profound. The ice also prevents oxygen getting into the water. This can be bad for animals if the ice persists.



Density (g/cm3)

Liq.	0.9984	0 °C
Ice	0.9168	0 °C

Water has several other unique physical properties. These properties are:

Water in a pure state has a neutral pH. As a result, pure water is neither acidic nor basic. Water changes its pH when substances are dissolved in it. Rain has a naturally acidic pH of about 5.6 because it contains natural derived carbon dioxide and sulfur dioxide.

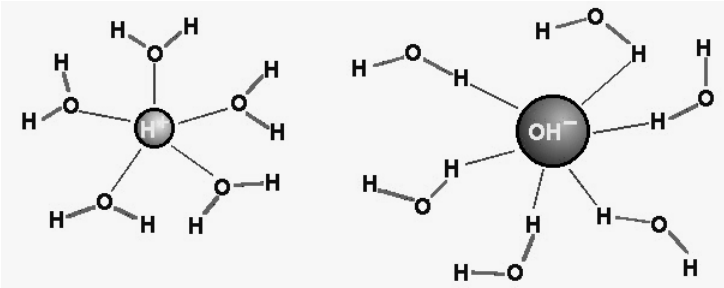
- L'acqua è *anfotera* (*anfolitica*, ovvero *anfiprotica*), cioè si comporta da acido o da base a seconda della natura della specie con la quale reagisce

- pH a 25 °C = 7

Una piccola parte delle molecole è **dissociata** secondo la reazione

$$H_2O \leftrightarrows H^+ + OH^-$$

Questa scrittura è una approssimazione semplicistica, poiché, in realtà, questi ioni (come tutti gli ioni in soluzione acquosa!) sono "solvatati" da altre molecole di acqua; sono cioè praticamente circondati dalla parte polare delle molecole circostanti che è di segno opposto rispetto alla carica dello ione.



In pratica potremmo scrivere, per esempio, in base alla figura,

$$12\ H_2O \leftrightarrows H_{11}O_5^+ + H_{13}O_7^-$$

ma, non potendo conoscere esattamente il numero di molecole coinvolte, non sarebbe possibile scrivere una formula corretta.

Per semplicità e per convenzione scriviamo perciò $2\ H_2O \leftrightarrows H_3O^+ + OH^-$

in cui H_3O^+ = ione idrossonio e OH^- = ione ossidrile

$\underline{K_w}$: costante relativa all'equilibrio di autoprotolisi dell'acqua.

È una costante a temperatura costante

Temperatura °C	**Kw**
0	**$1{,}139\times10^{-15}$**
10	**$2{,}920\times10^{-15}$**
25	**$1{,}000\times10^{-14}$**
50	**$5{,}474\times10^{-14}$**
80	**$2{,}340\times10^{-13}$**

- L'acqua pura (solo molecole di H_2O) praticamente non trasmette la corrente elettrica (conducibilità < 2 µS/cm)

Conducibilità: inverso della resistività. 1 µS/cm = 1 $\mu ohm^{-1} \cdot cm^{-1}$

Water conducts heat more easily than any liquid except mercury. This fact causes large bodies of liquid water like lakes and oceans to have essentially a uniform vertical temperature profile.

	20 °C	0 °C	0 °C Ice
thermal conductivity liquid (W/m*K)	0.5984	0.5610	2.240

Liquid water is a universal **solvent**. It is able to dissolve a large number of different chemical compounds. This feature also enables water to carry solvent nutrients in runoff, infiltration, groundwater flow, and living organisms.

Water has a high surface tension

- Tensione superficiale a 20 °C = 72,8 x 10^{-3} N/m

WATER PROPERTIES

Water is a transparent, odorless, tasteless liquid composed of the elements hydrogen and oxygen. Water is an universal solvent, meaning that many elements can be dissolved by water. Fresh water has relatively few elements dissolved in the water, while the oceans contain many dissolved salts.