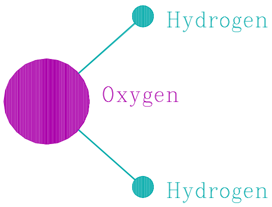
The properties of water

"From water does all life begin."

—OC Bible, 457 Kalima.

1. Static properties

The chemical formula of water is H_2O. Its molecular structure is roughly as shown below:



The density of water, at standard temperature and pressure is, by definition

$$\rho = 1\ \mathrm{gm/cm^3} = 10^3\ \mathrm{kg/m^3}\ .$$

Since the molecular weight of water (ignoring isotopes like ^{18}O and ^{2}H) is 18, the number density of molecules in liquid water is

$$n = \frac{N_A}{18} \approx 3\times10^{22}\ \mathrm{cm^{-3}}\ .$$

The spacing between the hydrogen and oxygen atoms in the molecule is about

$$r \approx 1\ \text{Å} \overset{df}{=} 10^{-8}\ \mathrm{cm}\ .$$

We may estimate the collision cross-section of a water molecule (with a point-like particle) as its geometric cross section:

$$\sigma \approx \pi r^2\ ;$$

the cross section for a collision between two such molecules is therefore about four times as large,

$$\sigma_{H_2O\text{–}H_2O} \approx 10^{-15}\ \mathrm{cm^2}\ .$$

The mean free path of a molecule (that is, the average distance it can travel between collisions) is therefore

$$\lambda = \frac{1}{n\,\sigma} \approx 2.5\ \text{Å}\ .$$

We can estimate the average inter-molecular spacing in liquid water by computing the volume per molecule (often called the *specific volume*):

$$\omega \overset{df}{=} \frac{1}{n} = \frac{4\pi}{3} r_0^3$$

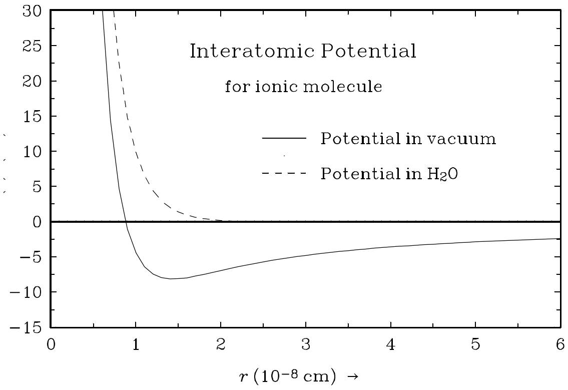
giving $r_0 \approx 2\ \text{Å}$, which means the inter-molecular spacing is $2r_0 = 4\ \text{Å}$. Thus the molecules in water are not actually touching each other (which is why it is a liquid rather than a solid) but they are very close together. The mean free path is smaller than the average inter-molecular spacing.

2. Solvent properties

Water has a very large dielectric constant, about 80 (times the dielectric constant of vacuum). Thus the Coulomb potential between—say—the atoms of the NaCl molecule (salt) is modified to

$$V_{H_2O} = \frac{-e^2}{\varepsilon\, r}$$

The interatomic potential looks like an attractive Coulomb potential at long distances, but has a short-ranged repulsive part, so the total looks something like the figure below:



The actual binding energy of the NaCl molecule is about 4.3 eV, but when the molecule is immersed in water and the Coulomb potential is reduced by a factor 80, the minimum of the potential is now of the order of the thermal energy at room temperature ($T \approx 300\,^{o}$K). That is, the molecule is essentially no longer bound.

3. Solubility of H2O in H2O

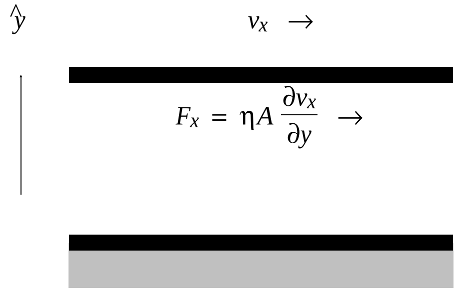
The title of this section sounds almost paradoxical—how can something dissolve itself? The interesting thing is that water does just that. The energy required to remove a hydrogen ion from a free water molecule is of the order of several eV. If that removal energy were the same for a water molecule in the liquid phase as for a gas molecule, the Boltzmann distribution would then predict that the fraction of H^+ ions in liquid water would be

$$e^{-\Delta E/kT} \approx e^{-80} \sim 10^{-35} .$$

However, liquid water has a pH of 7—meaning that the fraction of dissociated molecules is 10^{-7}. Hence we conclude the binding energy of the water molecule is very much less in the liquid environment than in the gas phase. Ergo, water dissolves water.

4. Viscosity

The viscosity of a liquid is defined as follows: consider two parallel plates of area A with a film of the liquid between them, as shown below:



The lower plate is fixed, the upper one is dragged at constant speed v_x in the x-direction. The force required to drag it is proportional to the area of the plates, the viscosity η of the liquid, and to the gradient of the relative velocity in the direction normal to the plates.

Objects moving at small speeds through liquid experience a viscous drag force proportional to and opposing their velocity. The force has the form

$$\vec{F} = -\Gamma a \vec{v} ,$$

where Γ is a geometric factor and a is the linear dimension. Thus for example, a sphere of radius r experiences the drag force (Stokes's Law)

$$F = -6\pi r \eta v .$$

We previously introduced the idea of *Reynolds's number*: an object of volume Ω and linear dimension r, moving through liquid of density ρ, has to impart velocity v to a mass $m = \Omega \rho$ in time $\delta t \approx r/v$. The inertial force it applies to the liquid is thus

$$F_{in} \approx \Omega \rho \frac{v^2}{r} .$$

On the other hand, the viscous force is

$$F_{visc} = \Gamma \eta v ;$$

The ratio of inertial to viscous force (stripped of geometric factors) is called *Reynolds's number*,

$$R \overset{df}{=} \frac{F_{in}}{F_{visc}} = \frac{\Omega \rho v^2}{\Gamma r^2 v \eta} \to \frac{\rho r v}{\eta} .$$

The viscosity of water in cgs units is about 0.01, hence for a barracuda of length 100 cm swimming at—say—10 m/sec (about 20 mi/hr) the Reynolds number is 10^7. Inertia dominates viscosity by an enormous factor.

But for an *E. coli* bacterium of dimension 10^{-4} cm, swimming at 3×10^{-3} cm/sec, the Reynolds number is 3×10^{-5}. Here viscosity dominates inertia by a large factor. We saw that the coasting distance for a bacterium that stops turning its propeller is

$$x_{stop} = \frac{2}{9}\frac{\rho r^2 v_0}{\eta}.$$

The stopping distance is 0.07 Å—about 0.07 of an atomic radius! For practical purposes, when a bacterium stops swimming it stops dead in the water.

5. Specific heat

The specific heat of water is defined by the heat required to raise the temperature of one gram by one degree Celsius. The heat required is the *calorie*, whose mechanical equivalent is about 4.2 Joule. Thus the molar specific heat of liquid water is 75.3 J, almost exactly $9R$ (R is the perfect gas constant, about 8.32 J/gm-mol/^{o}C).

Is there any easy way to see why this is so? The Law of Equipartition in thermodynamics says that the average thermal energy of a particle (say, an atom) is

$$\langle E\rangle = \frac{1}{2}k_BT$$

per "degree of freedom", where Boltzmann's constant is $k_B \overset{df}{=} R/N_A$. Now we count degrees of freedom as follows: each translational motion (and there are three, in 3-dimensional space) counts as one; each rotational mode counts as one; and each vibrational mode counts as two (because the average potential energy in a harmonic oscillator is the same as the average kinetic energy). Thus for a monoatomic gas the average energy per molecule is $\frac{3}{2}kT$ and the molar specific heat is $\frac{3}{2}R$.

As we have seen, the water molecule is triatomic. Its center of mass has 3 translational modes and since it has 3 large principal moments of inertia, there are 3 rotational modes. Additionally water has 3 (normal) modes of internal vibration. Two of them will have the same frequency (because of the symmetry) and the third will be much lower in frequency (because it involves a scissors motion of the hydrogen atoms, rather than the stretching of the strong oxygen-hydrogen bonds). Quantum mechanics says that vibrational modes cannot be excited until the temperature is high enough:

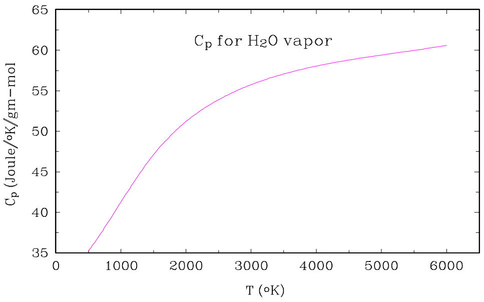
$$kT \approx \hbar\omega.$$

Moreover, from the perfect gas law we can deduce that the molar specific heat at constant pressure is the specific heat from the internal energy plus R.

Thus a gas of water molecules (water vapor or steam) should have molar specific heat at constant pressure increasing with temperature from $4R$ to $7R$. In fact, from tables we find for water vapor in the temperature range 100–500 ^{o}C

$$c_p \approx 4.5R,$$

so we are on the right track: the internal energy involves a bit more than 6 degrees of freedom (that is, a vibrational mode is partially excited). Below we see a plot of the specific heat of water vapor in the temperature range 400–6000 ^{o}K:



At the lowest temperature in the Figure the specific heat is $4.2R$, rising asymptotically to $7.5R$ at the upper end of the range. Since

$$c_P = \left.\frac{\partial U}{\partial T}\right)_P + R$$

we see that over this range the internal energy of a gas of water molecules can be written

$$U = \left(\frac{3}{2}R + \frac{3}{2}R\right)T + U_{vib}(T) + U_e(T)$$

where $U_{vib}(T)$ runs from slightly more than 0, to $3R$ (when the temperature is well above the vibrational excitation energy). At the highest temperature, we clearly begin to excite internal electronic states of the molecule. The lowest such excitation energy must be of the order of electron volts; since $1\ \mathrm{eV}/k_B = 12{,}000\ ^{\mathrm{o}}\mathrm{K}$, it should not surprise us that at 6000 $^{\mathrm{o}}$K such states begin to play a role in the thermodynamics[1] of water vapor.

But what about liquid water? Here the volume remains (more-or-less) constant, and the specific heat per molecule is $9k_B$, implying 18 degrees of freedom. How can this be?

Suppose water were really a solid. Then according to the law of Dulong and Petit we would expect—at sufficiently high temperature[2]—to find a specific heat of $3k_B$ per atom, or $9k_B$ per (triatomic) molecule. That is, this law would predict the molar specific heat of $9R$, which would imply that both the rotational and translational degrees of freedom of a given molecule are constrained by springs—intermolecular chemical bonds—and additionally, that the 3 *internal* vibrational states were being excited by thermal motions.

On the other hand, if the internal vibrational modes were not excited, the specific heat would be only $6R$. Now we have seen that for water *vapor*, at much higher temperatures, the internal vibrational modes are *not* excited. So how can they be excited in liquid water? The answer, once again, is the high dielectric constant of liquid water. As we saw in our discussion of pH, the effective spring constants between the atoms in a given molecule are weakened 80-fold, leading to an almost 9-fold decrease in the temperature at which they can be excited. That is, rather than lying at several thousand $^{\mathrm{o}}$K, the excitation temperature is depressed well below room temperature.

6. Heat of vaporization

The molecules of liquid water interact fairly strongly. Thus to break a molecule loose requires considerable energy. For water this so-called heat of vaporization is about[3] 540 cal/gm, or about 0.4 eV/molecule.

We can use the heat of vaporization to estimate the size of molecules. A molecule in a liquid interacts only with its nearest neighbors—say 6 of them, so its average potential energy will be roughly

$$\langle V \rangle \approx -6B$$

where B is the energy per bond. The energy of N molecules is therefore

$$E_{vol} \approx -6NB = -6B\frac{N}{\Omega}\Omega \equiv -6Bn\,\Omega\,,$$

where n is the number-density (assumed constant) and Ω is the volume. That is, the dominant contribution to the energy is proportional to the volume. However, this overcounts because the molecules at the surface have fewer neighbors than those in the interior, hence have fewer bonds. The number of surface molecules is

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[1] If the first elctron excitation has energy 2 eV, about 2% of the molecules will be excited at 6000 *o*K, raising the specific heat to $6.6R$.

[2] For many solids, “sufficiently high” is room temperature; however, for diamond, whose “springs” are stiffer than those of other materials, the specific heat at room temperature is substantially lower than that of other materials.

[3] The heat of vaporization is temperture dependent. At 0 $^{\mathrm{o}}$C it is closer to 600 cal/gm. The average is 573 cal/gm.

$$N_{surf} = nA\tau$$

where τ is the surface thickness and A the surface area. If we suppose the surface molecules have one fewer bond apiece, the correction is

$$E_{surf} \approx BN_{surf} = Bn\tau A \overset{df}{=} S A$$

where we have defined the *surface tension S* as the correction to the total energy from the surface of the body of water.

Now, suppose we could break up the entire volume of water into individual molecules. Wvidently this would require energy proportional to the total area: if the molecules are supposed little spheres of radius r, the total surface area is

$$A = N\, 4\pi r^2$$

and the energy required is[4]

$$\Delta E = SN\, 4\pi r^2.$$

If we let $N = N_A$ and set the energy equal to the vaporization energy per mole, we find

$$\frac{E_{vap}}{N_A} \approx S\, 4\pi r^2 .$$

The surface tension of water at 20 °C is about 73 erg/cm^2 so we find a radius of about 2.8 Å. If we had assumed cubic rather than spherical molecules the cubes would have been about 4 Å on a side.

From the above considerations we can ascribe a tensile strength to a column of water[5]. Imagine the water in a long thin column, and now break the column. The total area increases by twice the cross-sectional area, a, of the column, requiring an energy input

$$\Delta E = 2aS .$$

But if the force exerted falls from $f_{\max}$ to 0 over the distance τ, then we have

$$\Delta E = 2aS \approx \frac{1}{2} f_{\max}\, \tau .$$

Now we may re-express this in terms of the heat of vaporization and the volume per molecule:

$$Y_{\max} = \frac{f_{\max}}{a} = \frac{4S}{\tau} \approx \frac{2}{3}\,\frac{|E_{vap}|}{v}$$

where v is the molar volume. For water this number is then (in dynes/cm^2)

$$Y_{\max} \approx 0.67 \times 590 \times 4.2 \times 10^7 \text{ dyne/cm}^2$$

$$= 1.7{\times}10^{10} \text{ dyne/cm}^2 .$$

7. Vapor pressure

When water and water vapor coexist in thermal equilibrium at the same temperature, the number of molecules in the liquid, that in a given time randomly gain enough energy to escape, must be balanced by an equal number (on average) from the gas that inelastically collide with the surface and are captured. Thus thermodynamics leads to a relation between the partial pressure p_w of water vapor in saturated air above the surface of a body of water, and the molar heat of vaporization, E_{vap} :

$$p_w = p_0\, e^{-E_{vap}/RT} .$$

The constant p_0 depends on such things as the capture probability, which in turn depend on details of the interactions. That is, although p_0 could in principle be computed from the laws of quantum mechanics, in our present state of knowledge it remains an empirical constant. The correctness of

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[4] This area so greatly exceeds the area of a macroscopic contiguous body of fluid that we can ignore the energy associated with the latter.

[5] In order for this to be either meaningful or measurable we must put the water in a capillary tube to stabilize it so the sides do not neck in (as they would for a free strand of water) causing the strand to break.

this law is seen from the semi-logarithmic plot below: