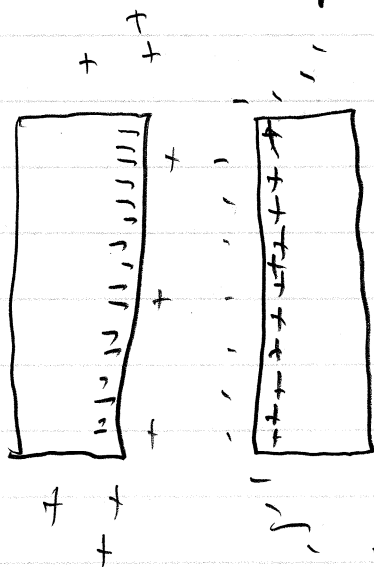


7.4.5 What if the surfaces are of opposite charge? Then at large separations both are neutral



and there is no long-range force.

But as they approach each other, their counterion clouds mingle and may leave the gap between the surfaces



The two clouds of counterions have more available volume, more

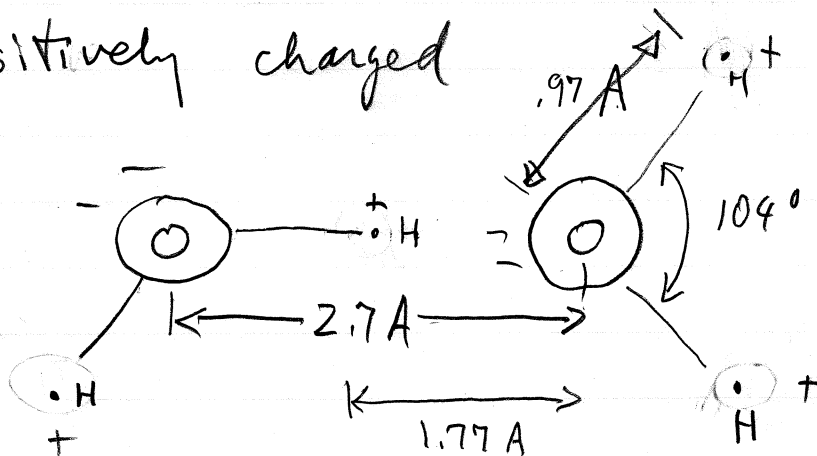
micro states, and so more entropy. So $F = E - TS$ goes down and the surfaces are shoved together.

Eventually, the two surfaces are nearly contiguous and the energy estimated in Eq. (7.27) is released

$$\frac{\Delta E}{A} = \frac{2\varepsilon}{A} = 2kT \frac{\sigma}{e}$$

which is very large. So when oppositely charged surfaces can sit together, they bind together very tightly.

Water molecules are electric dipoles. The oxygen atom is negatively charged, and the hydrogen atoms are positively charged

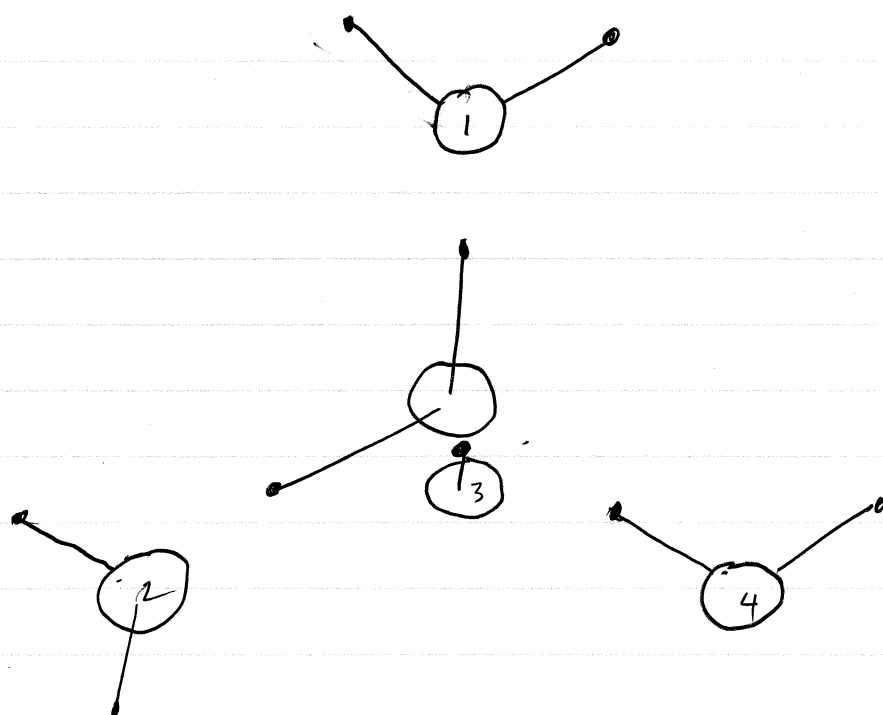


In a water molecule, the oxygen atom steals almost 100% of the company of the electron of each hydrogen atom.

So the H atoms in H_2O are approximately just protons. The electric field becomes extremely intense near

these naked protons. It's e/r^2 as

$$r \rightarrow 10^{-13} \text{ cm.}$$



1, 2, 3, 4 are corners of regular tetrahedron

These H-O bonds are called H-bonds or hydrogen bonds. Two water molecules in vapor are bound by -9 kT . Ordinary van der Waals bonds are $\sim 0.6 - 1.6 \text{ kT}$. Covalent bonds run from 90 to 350 kT.

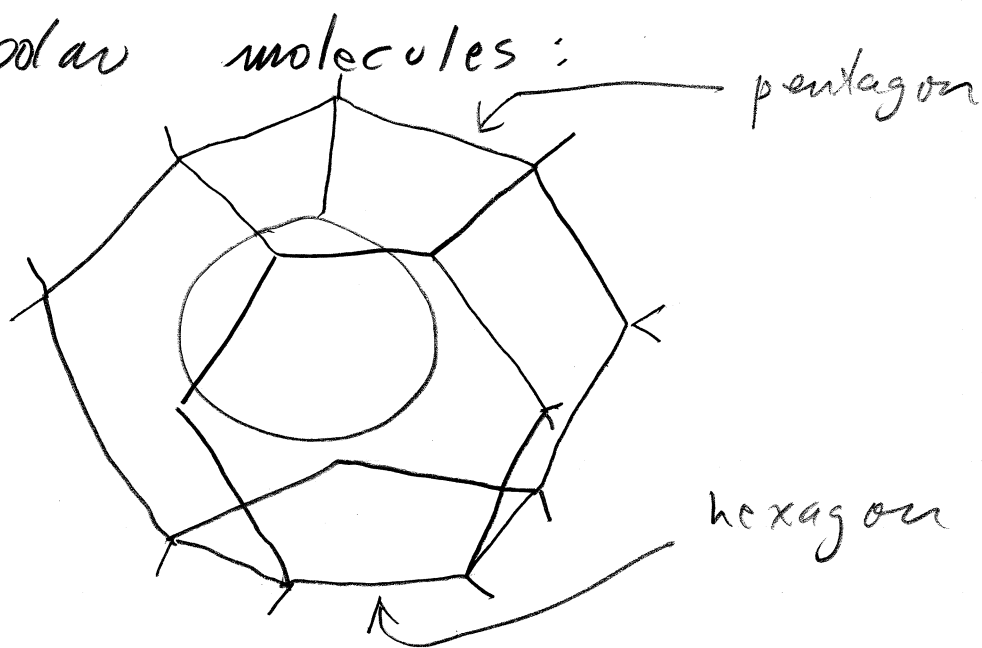
In water at room temperature, each water molecule manages to keep about 3.5 of the 4 H-bonds it has in ice. This is why the boiling point of water is 189 K higher than that of ethane $\text{CH}_3 - \text{CH}_3$. Methanol $\text{CH}_3 - \text{OH}$ makes fewer H-bonds per molecule and boils only 36 K below water.

N-H as well as O-H can form H-bonds. When one breaks in water, another easily forms, so the net free-energy cost is only $1-2 kT$, not $9 kT$.

Solubility: H_2O_2 dissolves well in water because it can make almost the same H-bonds. Sugar is less soluble in water, but still dissolves fairly well due to its OH groups. But hydrocarbons, fats, oils, and other non-polar molecules dissolve poorly in water.

Water molecules form

clathrate cages around small
non-polar molecules:



Most of the H-bonds of water are kept in a clathrate cage, but none of the H-bonds can point in at the non-polar molecule in the center. So each non-polar molecule raises $F = E - TS$ by breaking an H-bond, and so raising E , or by ordering the H-bonds, and lowering S .

The relative insolubility of nonpolar molecules is called the hydrophobic effect.

The solubility of heptanol $C_7H_{15}OH$ drops as T rises from $9^\circ C$ to $50^\circ C$ (Fig. 7.14) because the entropic cost $-ST$ rises with T .

H-bonds are of short range — about 2 \AA . So the hydrophobic effect is a surface effect. For propane C_3H_8 it's about $6kT$ for $2(\text{nm})^2$ or $3kT$ per $(\text{nm})^2$.

Large nonpolar objects have a similar surface free-energy cost when immersed in a polar solvent. But because water can't form a clathrate cage around a large object, many H-bonds do break and there is a large energy cost in the free-energy cost. But very roughly, the free energy per unit area is the same - at least the same order of magnitude. Thus the air-water interface has a free energy of

$$\frac{F}{A} \approx 0.072 \frac{J}{m^2}$$

per m^2 .

For propane

$$\frac{F}{A} = 3kT (\text{nm})^{-2} = 3 \times 4.1 \times 10^{-21} \times 10^{18} \text{ m}^{-2}$$

$$= 0.012 \text{ J m}^{-2}. \quad \leftarrow \boxed{7H}$$

Nonpolar solvents easily accept nonpolar solutes. Thus fatty acids, like hexanoic acid, and steroid or secosteroid hormones readily pass thru the lipid bylayers of cell membranes.

Water molecules can cause a depletion effect on their own. Thus large molecules with surfaces that fit well together can be held together by several short-range effects:

- (1) van der Waals attraction at $\lesssim 1 \text{ nm}$
- (2) H-bonds with a range of $\sim .2 \text{ nm}$
- (3) opposite charges or charge layers, which are screened at $\sim 1 \text{ nm}$.
- (4) the depletion effect with small molecules as "sheepdogs." Water molecules can act as sheepdogs. Here the range is $\sim 2R \gtrsim 0.2 \text{ nm}$.

Here's a simple way to think about osmotic pressure at equilibrium; The solvent molecules pass thru the membrane and so establish the same concentration c_w on both sides of the membrane. The solute molecules are stuck on one side at concentration c_s . So $\Delta p V = N_s k T$ or $\Delta p = \frac{N_s}{V} k T = c_s k T$.