Lecture 8: Chemical Equilibrium for the Autodissociation of Pure Water

One of the great things about college courses is that they tend to shake the foundation for the stuff you learned to be true in grade school. Like when you learned that the pH of pure water is 7. Today you will learn the truth, water rarely has a pH of 7.

Now the tool I will be using to come to this conclusion is our new found friend, chemical equilibrium. And pretty much all I am going to be doing in this lecture is taking a look at a single equilibrium in which water forms ions on its own.

Here is the chemical equilibrium:

$H_2O \rightleftharpoons H^+ + OH^-$ which has an equilibrium expression $K_w = [H^+][OH^-]$ (remember to not include the [H_2O] term)

To learn the truth about water's pH, we will use this equilibrium expression with some things you were taught in CH301 and the recent material on the RICE calculation.

Time out for pH:
As you have seen, K values can often become unwieldy with large positive and negative exponents. Likewise, the concentrations derived from calculations can be rather cumbersome—like 5.7 x 10^{-13}M. Now these days people can handle such numbers in calculators pretty easily, but in the old days, we tended to use log functions to simplify presentation and calculation. So the following idea was hatched to make things easier:

$$let \quad pX \equiv -\log[x]$$

as a way to simplify presentation of numbers and calculations. So a number like 1 x 10^{-7} when subjected to the p(1 x 10^{-7}) function yielded the number 7 by simply removing it from the exponent and changing the sign. And in general the pX function takes anything and turns it into –log, so

$$pH=-\log[H^+] \qquad pOH=-\log[OH^-] \qquad pK=-\log[K]$$

We do this so that numbers like

$1\times10^{-5} \qquad 1\times10^{-11} \qquad 1\times10^{-4.74}$

$\searrow p \qquad\qquad \searrow p \qquad\qquad \searrow p$

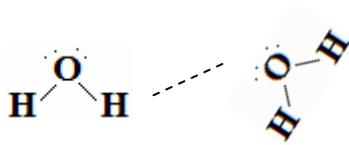$5 \qquad\qquad 11 \qquad 4.74$ become much simpler numbers to work with

Time in.

Creating a chemical basis for understanding why water dissociates.
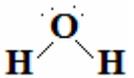
We   know H_2O (structure shown)   has polar covalent bonds and is relatively stable.
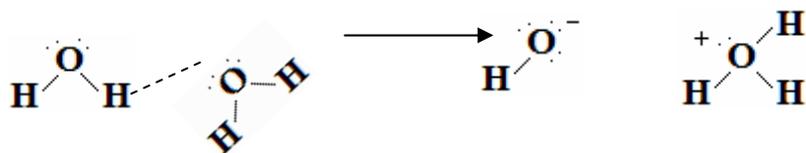
But we also know water   forms intramolecular forces through hydrogen bonds and that these forces can have a significant impact on neighboring species.

For example, recall that a salt crystal   has a strong lattice energy and yet it can still be attacked by pesky water molecules that try to hydrated ions. Well the same thing can happen, (to a much smaller degree, with water.) If we look at a large distribution of H_2O molecules in solution, there is a distribution of internal energies that depend on the temperature. Now at the tail, some small fraction of water molecules will have a lot of internal energy and will be more susceptible to being pulled apart by the intermolecular hydrogen bonding interactions. Not a lot, but some.

Some very small fraction dissociates because of the external H-bonding pull of adjacent waters
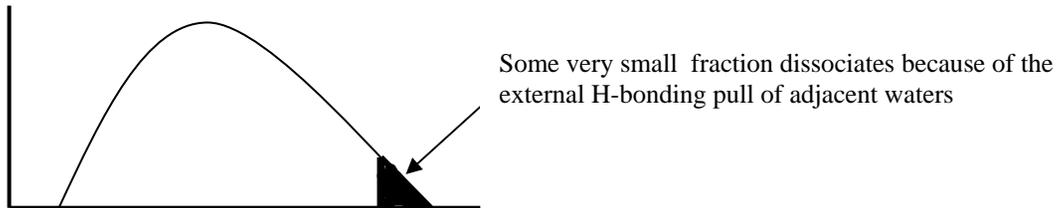
The chemical reaction that occurs is the autodissociation of water

Note the formation of ions, just like with a salt.

We can write this chemical equilibrium as

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$ where the H_3O^+ is a hydronium ion and the OH⁻ is a hydroxide ion.

Of course some chemists are profoundly lazy and never like to write the hydronium ion, but instead show just a proton, H^+

$$H_2O \rightleftharpoons H^+ + OH^-$$ and promise to remember that here is always water present.

So the question is, how many H_2O dissociate? And the answer should be, well, if it depends how many waters have a high enough internal energy, then the answer is that it depends on temperature. Which of course we know from thermodynamics anyway.

But we can set up a RICE expression and add the initial concentrations of each compound (note that pure water has a constant initial [ ])

1000 ml in 1L
→1000g in 1L
→1000/18=55.4 moles in 1L
→55.4 M

H_2O	$\rightleftharpoons$ H^+	$+ OH^-$
55.4M	0	0
− x	+ x	+ x
55.4M- x	x	x

A first approximation, 55.4M – x ≈ 55.4M because very little dissociation occurs.

And we set up the equilibrium expression, noting that the 55.4M is absorbed into the K value since it is for a pure liquid, and then substitute the [x] values from the equilibrium expression.

$$K_w = [H^+][OH^-] = (x)(x) = x^2$$

Now all we need is a K value and we can find the concentration of protons in water. Scientists determine thermodynamic and equilibrium values for a living and put them in books. Shown below are a range of different temperature dependent values for the autodissociation of water that you can find in better chemistry textbooks everywhere. Note that these are some pretty small values which suggest what we already know, water doesn't ionize easily.

T (°C)	K_w
0	0.114×10^{-14}
10	0.293×10^{-14}
20	0.681×10^{-14}
25	1.008×10^{-14}
30	1.471×10^{-14}
50	5.476×10^{-14}
100	51.3×10^{-14}

To keep you on firm ground for a little longer, let's do a calculation to find the actual number of $[H^+]$ in water using the K_w value at 25°C and solving that RICE expression.

So with

$$K_W = 1 \times 10^{-14} = [H^+][OH^-] = x^2$$

$$x = [H^+] = [OH^-] = 10^{-7}$$

so

$$H^+ = 1 \times 10^{-7}$$

$$pH = -\log[10^{-7}] = 7$$
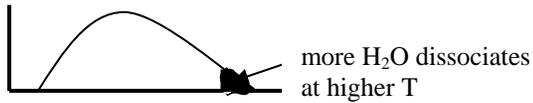
but H^+ also = OH^-, so pH = pOH= 7 as well.

And this is the source of the notion that pH of pure water is 7 when in fact, it is only about equal to a pH 7 when the temperature of the system is around 25°C.

**So what is happening to the pH of neutral water at other temperatures?**

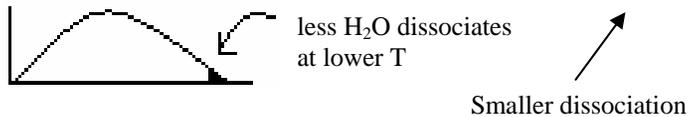Well consider hot water where the percentage of higher energy water is greater. More dissociation occurs.

$H_2O \rightleftharpoons H^+ + OH^-$ $K_w = \left[\overset{x}{H^+} \right]\left[\overset{x}{OH^-} \right] = 51 x 10^{-14}$

$x^2 = 51 \times 10^{-14}$
$x = [H^+] = [OH^-] = 7.14 \times 10^{-7}$
pH=pOH=6.14

more H_2O dissociates at higher T

Or what about cold water where the percentage of water molecules with the energy to dissociate is smaller.

$H_2O \rightleftharpoons H^+ + OH^-$ $K_w = \left[\overset{x}{H^+} \right]\left[\overset{x}{OH^-} \right] = 0.14 x 10^{-14}$
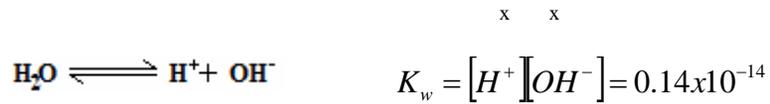
$x^2 = 0.14 \times 10^{-14}$
$[H^+] = [OH^-] = 3.7 \times 10^{-8}$
pH=pOH=7.42

less H_2O dissociates at lower T

Smaller dissociation

And for each of the temperatures below, you can quickly find the pH of the protons or hydroxides in pure water—it is just the square root of the K_w after assuming that very little dissociation occurs.

T (°C)	K_w	pH
0	0.114×10^{-14}	7.47
10	0.293×10^{-14}	7.27
20	0.681×10^{-14}	7.08
25	1.008×10^{-14}	7.00
30	1.471×10^{-14}	6.92
50	5.476×10^{-14}	6.63
100	51.3×10^{-14}	6.14

Some take home messages:

- The real definition of a neutral water solution is one in which the $H^+ = OH^-$ or pH = pOH
- Neutral water solutions can occur over a wide pH range from near pH 6 to pH 7.5 depending on the temperature.
- It is fun to walk up to friends who are drinking a glass of cold ice water and scream "of my gosh, you are drinking a glass of pH 7.5 water"
- As you spend hours studying what happens when you dump stuff in water over the next two months, remember that the dissociation equilibrium for water must always hold true— $K_w = [H^+][OH^-]$. It is just that H^+ will not equal OH^- if the solution is not neutral
- Your teachers lied to you about a lot of other stuff in grade school.