pH: Water.

A. Introduction

This handout starts a new series, which follows solutions. The general theme of the next few topics is pH (acidity).

In previous handouts you have learned how to make solutions that contain desired amounts (concentration) of solutes. One further characteristic of solutions that is often of interest is pH. pH is a measure of the "acidity" of the solution. In fact, pH does relate to concentration, but it's a more complex story.

In this handout we first talk about some properties of water that are necessary background to understanding pH. We then introduce pH, more or less as vocabulary at this point. In the following handouts of this series, we will discuss acids and bases. First, we discuss the strong acids and bases, for which pH is easily calculated. Then, we move on to the more common and more complex weak acids and bases. Finally, we discuss buffers, which are solutions that tend to control their own pH.

Along the way, we will discuss some K values, such as K_w and K_a. These introduce the topic of equilibrium constants. This is certainly a quite important topic in chemistry, but I think it is beyond this course. The specific K's encountered here are a valid and useful introduction to equilibrium, but they are not entirely typical. Be cautious about generalizing from these if you later move on to a more general discussion of chemical equilibrium. (As usual, if you have a special need/desire for more, see me.)

You may want to refer to the Calculator handout for help with exponential notation and logs.

B. Water

The water molecule is covalently bonded, but the bonds are quite polar (because O is much more electronegative than H). At a very low frequency, water ionizes…

(1) $H_2O\ (l) \rightleftarrows H^+(aq) + OH^-\ (aq)$

[An alternative way to write this is

(1a) $2\ H_2O\ (l) \rightleftarrows H_3O^+\ (aq) + OH^-\ (aq)$

Eq (1) shows release of H^+. In contrast, Eq (1a) shows transfer of H^+, in this case to another H_2O. One can argue that Eq (1a) is more rigorous. However, a simple view is that the two equations are equivalent, and H^+ (aq) and H_3O^+ (aq) represent the same chemical species. This simple view will serve our purposes here.]

The amount of ionization of water is small, less that 1 molecule out of 10^8. But it is measurable -- and important.

At "room temperature", the amount of water that ionizes is 1.0×10^{-7} M. Each water molecule that ionizes gives one of each kind of ion (Eq 1); therefore, it follows that the concentration of hydrogen ions is 1.0×10^{-7} M and the concentration of hydroxide ions is 1.0×10^{-7} M. For convenience, we use square brackets to mean "concentration of" (in molarity). Thus…

Key message: In pure water at 25 °C…

(2) $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M

You can accept the previous statement without any other background. However, I encourage you to review your basic chemistry book about the nature of water.

C. $[H^+]$ and $[OH^-]$ can vary…

If something is dissolved in the water, then Eq (2) may not hold. $[H^+]$ and $[OH^-]$ can have other values, besides 10^{-7} M. (We will discuss why in more detail later, but you may already be aware of acids and bases in general; acids raise $[H^+]$, bases raise $[OH^-]$.)

In fact, $[H^+]$ and $[OH^-]$ can have any value (at least over a very wide range, such as about 10^{-15} M to 10 M).

D. … but not independently

Extensive observation of aqueous solutions has led to the realization that whenever $[H^+]$ increases then $[OH^-]$ decreases -- and vice versa. In fact, the two concentrations are inversely proportional. More specifically:

In any aqueous solution at 25 °C, the product of $[H^+]$ and $[OH^-]$ is always $1.0 \times 10^{-14}\ M^2$…

(3) $[H^+][OH^-] = 1.0 \times 10^{-14}\ M^2$

The ion product, $[H^+][OH^-]$, is called the equilibrium expression. The value $1.0\text{x}10^{-14}\ M^2$ is called the equilibrium constant for the ionization of water, or, more briefly, the water constant, or, even more briefly, K_w…

(3a) $K_w \equiv [H^+][OH^-] = 1.0\text{x}10^{-14}\ M^2$

<u>To do</u>: Check that this holds for pure water; see Eq (2).

The K_w relationship is important. If we know $[H^+]$, we can calculate $[OH^-]$ -- or the reverse. The first set of problems is on just that.

If the concentrations are round powers of 10, you should be able to do the problems in your head. That is sufficient to establish the principle. In the real world, most concentrations are not round numbers. Use your scientific calculator for these; if you need help with exponents, see the early Calculator handout.

> (The general relationship of Eq (3) is universal, but the numeric value of K_w is a function of temperature. We will work here at "room temperature", ~20-25 °C, where K_w conveniently is a round number. If you need to work far from room temperature, check the value of K_w in a handbook.)

<u>Problems</u>

Problems marked with a * are more difficult, or introduce new material.

> (If you want to plan ahead, you might set up a table for these problems. For now, you need only two columns: $[H^+]$ and $[OH^-]$.)

1. If $[H^+] = 10^{-7}$ M, what is $[OH^-]$?
2. If $[OH^-] = 10^{-4}$ M, what is $[H^+]$?
3. If $[H^+] = 10^{-4}$ M, what is $[OH^-]$?
4. If $[H^+] = 10^{-12}$ M, what is $[OH^-]$?
5. If $[OH^-] = 10^{-2}$ M, what is $[H^+]$?
6. If $[OH^-] = 10^{-14}$ M, what is $[H^+]$?
7. If $[OH^-] = 10^{-15}$ M, what is $[H^+]$?
8. What is $[H^+]$ if $[OH^-] = 2.4\text{x}10^{-9}$ M?
9. What is $[OH^-]$ if $[H^+] = 1.8\text{x}10^{-3}$ M?
10. What is $[H^+]$ if $[OH^-] = 7.1\text{x}10^{-2}$ M?
11. What is $[OH^-]$ if $[H^+] = 5.7\text{x}10^{-11}$ M?
12. What is $[OH^-]$ if $[H^+] = 6.3\text{x}10^{-4}$ M?
13. $[OH^-] = 5.0\text{x}10^{-13}$ M. What is $[H^+]$?
14. $[OH^-] = 5.0\text{x}10^{-15}$ M. What is $[H^+]$?
15. $[OH^-] = 5.0$ M. What is $[H^+]$?

* 16. You have a solution which has $[H^+] = 10^{-7}$ M. You take 10 mL of this solution and add enough water to reach 100 mL total volume. What is $[H^+]$ after the dilution?
* 17. How many moles are in 1.00 L of water?

E. pH

The previous equations show chemical relationships. The statement that $[H^+] = 1.0 \times 10^{-7}$ M (Eq 2) is a statement of a chemical fact, based on observation. Similarly, Eq (3) expresses a relationship between two concentrations that is based on observing many aqueous solutions.

We now introduce pH. pH is another way to express $[H^+]$…

(4) $\text{pH} \equiv -\log[H^+]$

This is a definition. It involves no new chemistry, but merely a little math. $[H^+]$ is important, but the complicated numbers, usually with negative exponents, are a nuisance. So we define another value, a simple function of $[H^+]$ but with "nicer" numbers. Most pH values are between 0 and 14, and they are usually given with 1 or 2 decimal places. (The logs are base 10, common logs.)

Examples

1. $[H^+] = 10^{-7}$ M.

$\text{pH} = -\log[H^+] = -\log(10^{-7}) = -(-7) = 7.$

2. $[H^+] = 2 \times 10^{-3}$ M.

$\text{pH} = -\log[H^+] = -\log(2 \times 10^{-3}) = -(-2.7) = 2.7.$

Eq (4) shows how to calculate pH from $[H^+]$. You can also do the reverse, calculate $[H^+]$ from pH…

(5) $[H^+] = \text{antilog}(-\text{pH}) = 10^{-\text{pH}}$

Example

pH = 6

$[H^+] = 10^{-6}$ M

As before, you can do these in your head for simple powers of 10: the log of 10^N is simply N. But if the number has a coefficient, use your scientific calculator. Sect E of the Calculator handout contains a brief discussion of how to use your calculator for logs (and antilogs).

Of course, you already know how to interconvert $[OH^-]$ and $[H^+]$. Now you know how to interconvert pH and $[H^+]$. As a result, you are now able to convert from any one of these three parameters to any other -- in one step or two.

Example

pH = 5

$[H^+] = 10^{-5}$ M (from Eq 5)

$[OH^-] = 10^{-9}$ M (from Eq 3)

Problems

For each problem in Sect D, calculate the pH. (If you are using a table for the problems, just add one more column, for pH.)

As a separate problem set, do the reverse. Take each pH in the answer section, and calculate the $[H^+]$ and $[OH^-]$.

* 18. By how much (in units of M) does $[H^+]$ increase in going from pH 3 to pH 2?
19. Continuing… from pH 2 to pH 1?

Quiz. As suggested above, given any one of the three interrelated parameters ($[H^+]$, $[OH^-]$, and pH), you should be able to calculate the other two.

F. pThis and pThat [optional]

Chemists have generalized on the definition of pH. pThis ≡ -log(This). For example, we discussed K_w above. We can define $pK_w \equiv -\log(K_w)$. At 25 °C, $K_w = 1.0\text{x}10^{-14}$; therefore $pK_w = 14.0$.

We can also define $pOH \equiv -\log[OH^-]$. This is less commonly used than pH. However, the relationships between $[H^+]$, $[OH^-]$, pH and pOH are interesting. They all convey the same information, just in different forms. If you know any one of these four values, you can calculate the other three.

Optional problems: Calculate the pOH for each solution in the previous problems. (Just add another column to your table.) Look at the relationship between pH and pOH; this relationship can be easily derived from the equations in this handout. (The pOH answers are in the Table version of the answer set, below.)

If you have the Cracolice book, look at Fig 18.3, to see how these four parameters interrelate.

G. Answers

(A table version is also available for #1-15; see below.)

1. $[OH^-] = 10^{-7}$ M
2. $[H^+] = 10^{-10}$ M
3. $[OH^-] = 10^{-10}$ M
4. $[OH^-] = 10^{-2}$ M
5. $[H^+] = 10^{-12}$ M
6. $[H^+] = 10^{0}$ M (=1 M)
7. $[H^+] = 10^{+1}$ M (=10 M)
8. $[H^+] = 4.2\text{x}10^{-6}$ M
9. $[OH^-] = 5.6\text{x}10^{-12}$ M
10. $[H^+] = 1.4\text{x}10^{-13}$ M
11. $[OH^-] = 1.8\text{x}10^{-4}$ M
12. $[OH^-] = 1.6\text{x}10^{-11}$ M
13. $[H^+] = 2.0\text{x}10^{-2}$ M
14. $[H^+] = 2.0$ M
15. $[H^+] = 2.0\text{x}10^{-15}$ M
16. $[H^+]$ is still 10^{-7} M. Why? Because it is part of a chemical equilibrium, Eq (1). No acid or base were present, either before or after dilution. The solvent is neutral water, and has $[H^+] = 10^{-7}$ M in either case.

17. 55.6 (You did remember that 1.00 mL of water weighs 1.00 g??? In any case, the result is that pure water is ~56 M. Since $[H^+] = 10^{-7}$ M, you can see that the fraction of water molecules that is ionized is $<10^{-8}$, as stated earlier.)

Sect E: (1-16 are pH values.)

1. 7
2. 10
3. 4
4. 12
5. 12
6. 0
7. -1
8. 5.38
9. 2.74
10. 12.85
11. 10.24
12. 3.20
13. 1.70
14. -0.30
15. 14.70
16. 7.0

18. 0.009 M (10^{-2} M - 10^{-3} M)
19. 0.09 M (Compare with previous question. A 1 pH unit change is a factor of 10. The absolute amount of the change depends on the absolute concentration.)

The following table shows the $[H^+]$, $[OH^-]$, and pH for #1-15. The information originally given is in **bold**. The other entries were for you to calculate, in Parts D, E & F.

#	$[H^+]$	$[OH^-]$	pH	pOH
1	**10^{-7} M**	10^{-7} M	7	7
2	10^{-10} M	**10^{-4} M**	10	4
3	**10^{-4} M**	10^{-10} M	4	10
4	**10^{-12} M**	10^{-2} M	12	2
5	10^{-12} M	**10^{-2} M**	12	2
6	10^{0} M (=1 M)	**10^{-14} M**	0	14
7	10^{+1} M (=10 M)	**10^{-15} M**	-1	15
8	$4.2\text{x}10^{-6}$ M	**$2.4\text{x}10^{-9}$ M**	5.38	8.62
9	**$1.8\text{x}10^{-3}$ M**	$5.6\text{x}10^{-12}$ M	2.74	11.26
10	$1.4\text{x}10^{-13}$ M	**$7.1\text{x}10^{-2}$ M**	12.85	1.15
11	**$5.7\text{x}10^{-11}$ M**	$1.8\text{x}10^{-4}$ M	10.24	3.76
12	**$6.3\text{x}10^{-4}$ M**	$1.6\text{x}10^{-11}$ M	3.20	10.80
13	$2.0\text{x}10^{-2}$ M	**$5.0\text{x}10^{-13}$ M**	1.70	12.30
14	2.0 M	**$5.0\text{x}10^{-15}$ M**	-0.30	14.30
15	$2.0\text{x}10^{-15}$ M	**5.0 M**	14.70	-0.70