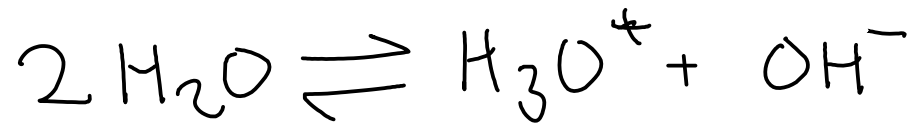
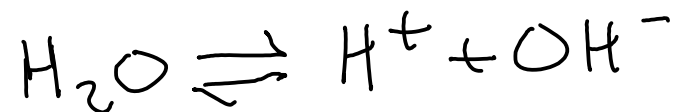


WATER CHEMISTRY

- Water self-ionizes!



or



This is an equilibrium reaction!

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

(X) = molar concentration of "X"

In aqueous solution, (H_2O) is essentially constant, so we roll that into K.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

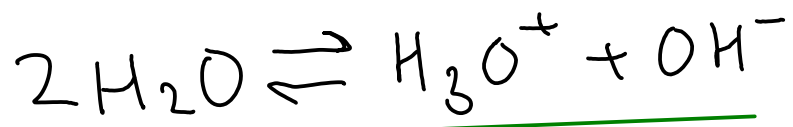
This is the value at 25C

WATER CHEMISTRY

- The self-ionization of water has a small equilibrium constant. What does this imply?

THE CONCENTRATION OF HYDROXIDE AND HYDRONIUM ION IN PURE WATER IS VERY SMALL!

How small?



In pure water, the concentration of hydroxide and hydronium must be equal, since they are formed at the same time and at the same ratio from the ionization reaction of water.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$$

Solve...

Let 'x' equal the change in concentration of hydronium ion...

$$(x)(x) = 1.0 \times 10^{-14}$$

$$x^2 = 1.0 \times 10^{-14}$$

$$x = 1.0 \times 10^{-7} \text{ M} = [\text{H}_3\text{O}^+] = [\text{OH}^-]$$

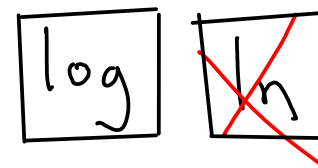
"p" NOTATION

- "p" notation helps us deal with the very small numbers we encounter when working with acids, bases, and water.

- based on log base 10

"p" means $-\log_{10}$

On a calculator, use



So,

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

$$\text{pOH} = -\log_{10} [\text{OH}^-]$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

"p" NOTATION

- Apply "p" notation to the water self-ionization reaction!

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

becomes ...

$$pK_w = \text{pH} + \text{pOH} = 14.00$$

Taking the "p" (negative log base ten) of the equilibrium constant is often used for BUFFER SOLUTIONS, which we'll discuss later!

ACIDITY AND ALKALINITY

- At $\text{pH} = 7$, $\text{pH} = \text{pOH}$. The solution is considered NEUTRAL

↳ Also, $[\text{H}^+] = [\text{OH}^-]$!

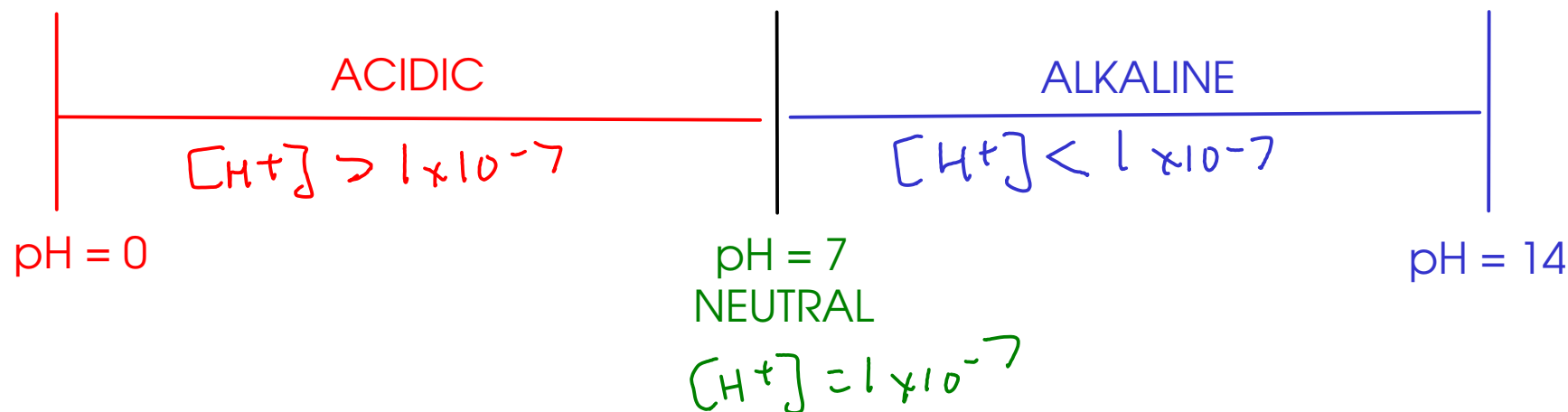
- At $\text{pH} < 7$, $\text{pH} < \text{pOH}$. The solution is considered ACIDIC

↳ Also, $[\text{H}^+] > [\text{OH}^-]$!

- At $\text{pH} > 7$, $\text{pH} > \text{pOH}$. The solution is considered ALKALINE (BASIC)

↳ Also, $[\text{H}^+] < [\text{OH}^-]$!

The pH scale...



pH AND TEMPERATURE

$$pK_w = pH + pOH = 14.00$$

This equation is valid at room temperature, specifically 25°C.

Equilibrium constants depend on TEMPERATURE, and change with temperature.

So, the "neutral" pH (where the concentration of hydroxide and hydronium ions are equal) CHANGES with changing temperatures

This change is important at temperatures greatly different from 25°C.

As an example, consider average "normal" human body temperature: 37°C

$$\text{At } 37^\circ\text{C}, \quad pK_w = 13.60$$
$$pH \text{ of neutral solution} = \underline{\underline{6.8}}$$

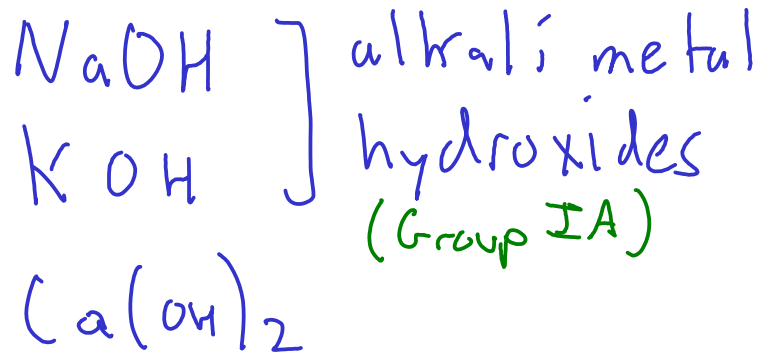
ACID-BASE EQUILIBRIUM IN WATER

- Like other ELECTROLYTES, acids and bases IONIZE to some extent in water
- STRONG electrolytes ionize completely. Acids and bases that ionize completely in water are called STRONG ACIDS and STRONG BASES
- WEAK electrolytes ionize partially, remaining mostly non-ionized. Acids and bases that ionize only partially in solution are called WEAK ACIDS and WEAK BASES.
- Most acids and bases are WEAK!

Common strong acids

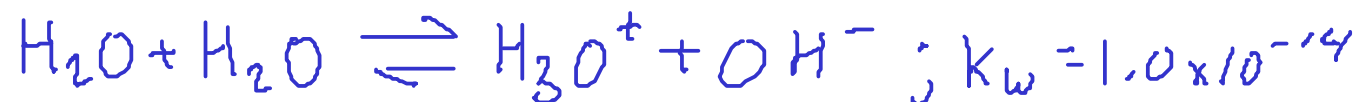


Common strong bases

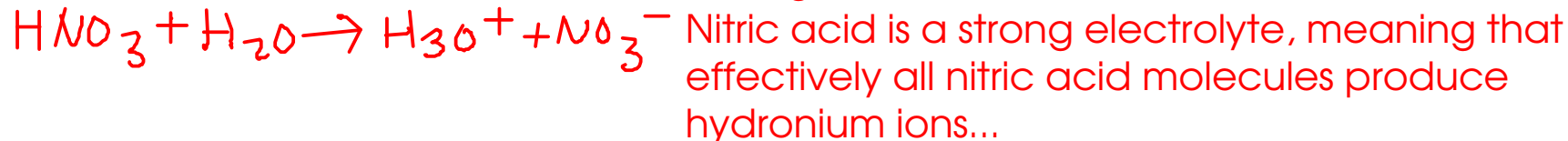


SIMPLE pH CALCULATIONS: STRONG ELECTROLYTES

- With strong acids and bases, the acid or base completely ionizes in water. So, we only have to worry about the effect of the acid or base on the water equilibrium itself.
- Since the equilibrium constant for the self-ionization of water is so small, the strong acid or base will overpower the hydronium (for acids) or hydroxide (for bases) produced by the water.



Consider a solution of 0.025 M nitric acid (a strong acid):



The ionization of the acid will produce 0.025 M hydronium ion, and this hydronium ion will suppress water's own ionization (by Le Chateleur's Principle). So we can effectively ignore water's equilibrium here and assume the concentration of hydronium ion is set by the hydronium production of the strong acid.

$$[\text{H}_3\text{O}^+] = [\text{HNO}_3] = 0.025 \text{ M}, \text{ so } \text{pH} = -\log(0.025) = \boxed{1.60}$$

Let's look at the amount of hydronium water would produce under these conditions and see if it's really ignorable. Find $[\text{OH}^-]$, which will be equal to the amount of hydronium ion the water itself makes (since each time water make a hydroxide it HAS to make a hydronium ion!)

$$(0.025) [\text{OH}^-] = 1.00 \times 10^{-14} \quad ([\text{H}_3\text{O}^+] [\text{OH}^-] = 1.0 \times 10^{-14})$$

$$[\text{OH}^-] = 4.0 \times 10^{-13} \text{ M} = [\text{H}_3\text{O}^+] \text{ produced by water!}$$

Consider a solution of 0.0125 M sodium hydroxide (a strong base):



The NaOH ionizes completely, meaning that essentially all NaOH is converted to hydroxide ion.



As before, the presence of one of the products of water's ionization will suppress water's own ionization. (The strong base provides hydroxide instead of hydronium, but the effect on water's ionization is the same!) We will assume that effectively all the hydroxide ion comes from the NaOH and ignore water's own production.

$[\text{OH}^-] = [\text{NaOH}] = 0.0125 \text{ M OH}^-$ Now we need to find pH

$$\text{pOH} = -\log(0.0125 \text{ M}) = 1.90 \quad (\text{pOH} = -\log[\text{OH}^-])$$

$$\text{pH} + 1.90 = 14.00 \quad (\text{pH} + \text{pOH} = 14.00)$$

$$\text{pH} = \boxed{12.10}$$

As before, let's check our assumption that the hydroxide concentration from the water itself really *is* ignorable. Find the hydronium ion concentration...

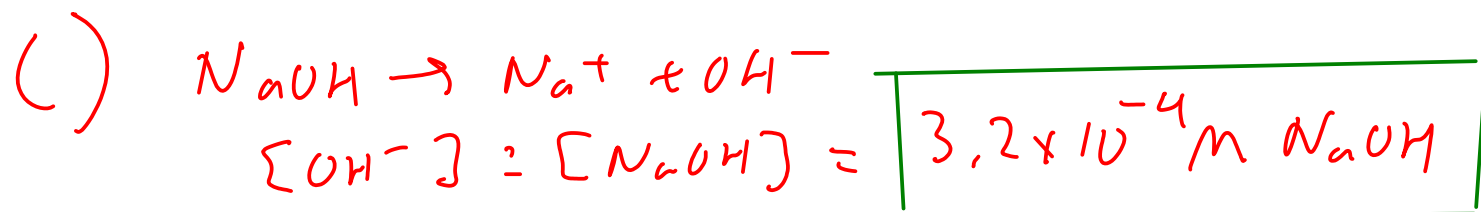
$$\begin{aligned} [\text{H}_3\text{O}^+] &= 10^{-12.10} = 7.9 \times 10^{-13} \text{ M H}_3\text{O}^+ \quad ([\text{H}_3\text{O}^+] = 10^{-\text{pH}}) \\ &= 7.9 \times 10^{-13} \text{ M OH}^- \text{ made by water} \end{aligned}$$

So the amount of hydroxide produced by water is indeed small enough to ignore compared to 0.0125 M hydroxide made by the base!

(A) What is the concentration of hydronium ion in an aqueous solution whose pH is 10.50? (B) What is the hydroxide ion concentration? (C) What molar concentration of sodium hydroxide solution would provide this pH?

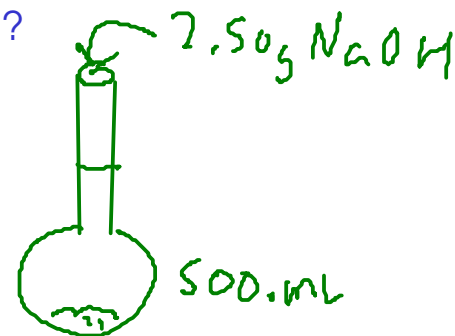
$$A) [H_3O^+] = 10^{-10.50} = \boxed{3.2 \times 10^{-11} \text{ M } H_3O^+} \quad ([H_3O^+] = 10^{-\text{pH}})$$

$$B) (3.2 \times 10^{-11} \text{ M}) [OH^-] = 1.00 \times 10^{-14} \quad ([H_3O^+][OH^-] = 1.00 \times 10^{-14})$$
$$[OH^-] = \boxed{3.2 \times 10^{-4} \text{ M } OH^-}$$



What is the pH of a sodium hydroxide solution made from dissolving 2.50 g of sodium hydroxide in enough water to make 500.0 mL of solution?

$$\text{NaOH: } 40.00 \text{ g/mol}$$



To answer this question, we'll need to find the molarity of NaOH solution.

$$2.50 \text{ g NaOH} \times \frac{\text{mol NaOH}}{40.00 \text{ g NaOH}} = 0.0625 \text{ mol NaOH}$$

$$M = \frac{\text{mol NaOH}}{\text{L solution}} = \frac{0.0625 \text{ mol NaOH}}{0.5000 \text{ L}} = 0.125 \text{ M NaOH}$$

↑ (from 500.0 mL)



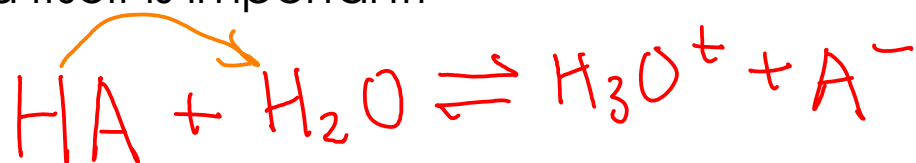
$$\text{pOH} = -\log(0.125 \text{ M}) = 0.90 \quad (\text{pOH} = -\log[\text{OH}^-])$$

$$\text{pH} + 0.90 = 14.00$$

$$\text{pH} = \boxed{13.10}$$

$$(\text{pH} + \text{pOH} = 14.00)$$

For a WEAK ACID, equilibrium does not lie far to the right. The ionization equilibrium of the acid itself is important!



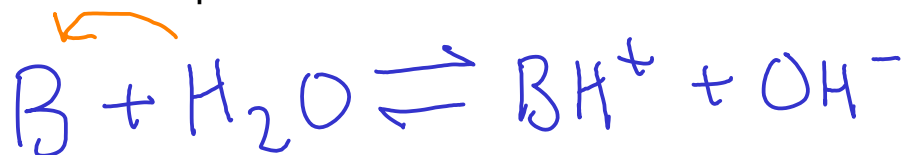
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

acid ionization constant

Again, water's concentration will not change significantly, so it is folded into the ionization constant

(HA) = concentration of undissociated acid

For a WEAK BASE, equilibrium does not lie far to the right. The ionization equilibrium of the base itself is important!



$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

base ionization constant

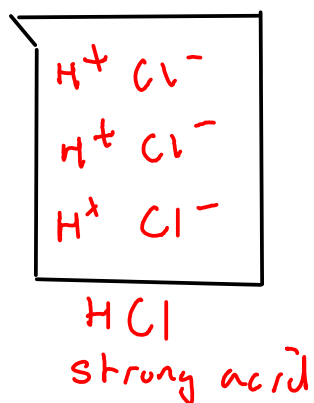
Values for K_a and K_b can often be found in data books / tables / or on the web.

In Ebbing, this data is in the appendices, on pages A-13 and A-14

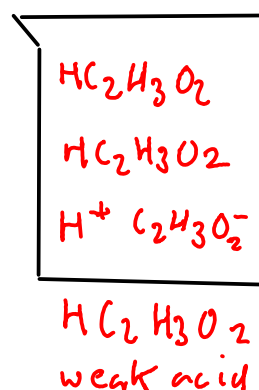
WEAK ELECTROLYTES

- In solutions of weak acids or bases, the UNDISSOCIATED form is present in significantly high concentration.

- The pH of a solution of weak acid will be HIGHER than the pH of a strong acid solution with the same nominal concentration!



VS



Fewer molecules of the weak acid ionize, so the concentration of hydrogen/hydronium ion is lower, meaning a higher pH!

- The pH of a solution of weak base will be LOWER than the pH of a strong base solution with the same nominal concentration!

Consider a 0.100M solution of nitrous acid, a WEAK ACID (HNO_2)



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = 4.5 \times 10^{-4}$$

Found on page A-14 in Ebbing 10th edition. These K values are determined experimentally like other equilibrium constants.

What is the pH of the solution?

This time, we'll need to solve the nitrous acid equilibrium to find out the hydronium ion concentration. We know how to do that, since it's just like the problems we worked in Chapter 14!

Species	[Initial]	Δ	[Equilibrium]
H_3O^+	0	+X	X
NO_2^-	0	+X	X
HNO_2	0.100	-X	0.100 - X

Let "x" equal the change in hydronium ion concentration

$$\frac{(x)(x)}{0.100 - x} = 4.5 \times 10^{-4}$$

$$\frac{x^2}{0.100 - x} = 4.5 \times 10^{-4}$$

$$\frac{x^2}{0.100 - x} = 4.5 \times 10^{-4}$$

We can solve this with the quadratic formula, but there's a simpler way ...

If $x \ll 0.100$, then
 $0.100 - x \approx 0.100$

$$\frac{x^2}{0.100} = 4.5 \times 10^{-4}$$

$$x^2 = 4.5 \times 10^{-5}$$

$$x = 0.0067082039 = [\text{H}_3\text{O}^+]$$

$$\text{pH} = \boxed{2.17} \quad (\text{Using the quadratic formula to solve gives a pH of about 2.19})$$

This is a quadratic, We can solve it with the quadratic equation:

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

When can we assume x is small enough to ignore in a subtraction? When the initial concentration of acid or base is 1000 times (or more) K_a or K_b .