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.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \; ; \; K_w = 1.0 \times 10^{-14}$$

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

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$

Assume that all the hydronium ion in solution is produced by the nitric acid, since the presence of the acid should suppress the self-ionization of water. (Le Chateleir's Principle)

So, $[H_3O^+] = [HNO_3]_{nominal} = 0.025\,M\ H_3O^+$

$pH = -\log_{10}(0.025) = \boxed{1.60}$ *

* For logarithms, the significant digits are BEHIND the decimal point. The numbers in front represent the EXPONENT in the original number, and are not significant

What would the HYDROXIDE ion concentration be under these conditions?

$[H_3O^+][OH^-] = 1.0 \times 10^{-14}$

$(0.025)[OH^-] = 1.0 \times 10^{-14}$

$[OH^-] = 4.0 \times 10^{-13}\,M$

... this also equals the hydronium concentration produced by water itself. And it's REALLY small compared to 0.025 M !

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

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

Like before, we'll assume all of the HYDROXIDE ion in solution comes from the sodium hydroxide (the strong base). We expect the presence of hydroxide from the base to suppress self-ionization of water.

$$[OH^-] = [NaOH]_{nominal} = 0.0125\ M\ OH^-$$

We'd like to know pH. First, find pOH.

$$pOH = -\log_{10}(0.0125) = 1.903$$

... then use the fact that pH and pOH are related by the water equilibrium.

$$pH + pOH = 14.00$$

$$pH + 1.903 = 14.00$$

$$\boxed{pH = 12.10}$$

Let's check the concentration of HYDRONIUM ion, since that will tell us how much water self-ionizes under these conditions. (Remember, we assumed this amount was very small compared to 0.0125 M)

$$[H_3O^+] = 10^{-pH} = 10^{-12.10}$$

$$[H_3O^+] = 8.0 \times 10^{-13}\ M$$

... this number also equals the amount of hydroxide ion produced by water itself, and is extremely small compared to 0.0125 M ...

(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) $pH = 10.50$, $[H_3O^+] = ?$

$10^{-pH} = [H_3O^+] = 10^{-10.50}$

$[H_3O^+] = \boxed{3.2 \times 10^{-11}\ M\ H_3O^+}$

B) $[H_3O^+][OH^-] = 1.0 \times 10^{-14}$

$(3.2 \times 10^{-11})[OH^-] = 1.0 \times 10^{-14}$

$[OH^-] = \boxed{3.2 \times 10^{-4}\ M\ OH^-}$

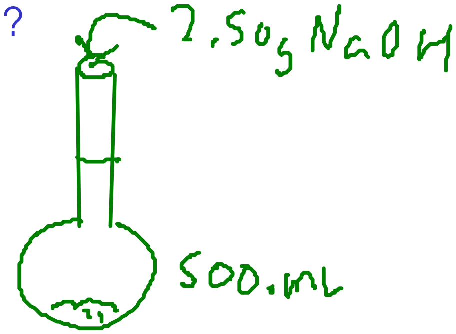
C) $NaOH \rightarrow Na^+ + OH^-$

1:1 ratio of NaOH to OH^-, so

$\boxed{[NaOH]_{nominal} = 3.2 \times 10^{-4}\ M}$ (0.00032 M)

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?

$NaOH: 40.00\ g/mol$



$$M = \frac{mol\ NaOH}{L\ solution} \leftarrow 0.500\ L$$

Find concentration of NaOH ... get the moles NaOH first:

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

$$M = \frac{mol\ NaOH}{L\ solution} = \frac{0.0625\ mol\ NaOH}{0.500\,L} = 0.125\ M\ NaOH$$

Since NaOH is a strong base, it will completely ionize and control the hydroxide concentration:

$$NaOH \rightarrow Na^+ + OH^-, \text{ so } [OH^-] = [NaOH]_{nominal}$$

$$[OH^-] = 0.0125\ M$$

$$[H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

$$[H_3O^+](0.0125) = 1.0 \times 10^{-14}$$

$$[H_3O^+] = 8.0 \times 10^{-14}\ M$$

$$\boxed{pH = 13.10}$$

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

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$\underbrace{K_a}_{\text{acid ionization constant}} = \frac{[H_3O^+][A^-]}{\underbrace{[HA]}_{\text{(HA) = concentration of undissociated acid}}}$$

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

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

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$\underbrace{K_b}_{\text{base ionization constant}} = \frac{[BH^+][OH^-]}{[B]}$$

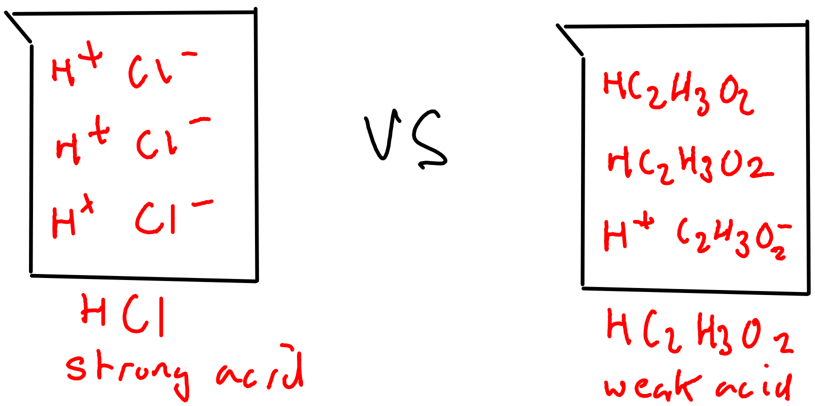
Values for Ka and Kb can often be found in data books / tables / or on the web.

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!



Fewer molecules of the weak acid ionize, so the concnetration 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)

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$$

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = 4.5 \times 10^{-4}$$

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

What is the pH of the solution?

To find pH, we need to determine the hydronium ion concentration at equilibrium. This time, we can't assume all the acid ionizes. So we'll need to solve the equilibrium problem for the acid's ionization:

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

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

This is very similar to the equilibrium problems we worked in Chapter 14!

$$\frac{(x)(x)}{(0.100-x)} = 4.5\times10^{-4}$$

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

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

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

$$\frac{x^2}{0.100-x} = 4.5\times10^{-4}$$

Ka is small, so there will be only a small amount of acid that ionizes. That means 'x' (which represents the amount of acid that ionizes) is also small. If 'x' is small relative to 0.100, then ...

$$0.100 - x \approx 0.100$$

When is it safe to assume that 'x' is small enough to drop from the subtraction term? When the initial concentration of acid or base is 1000x larger than the value of K ...

$$\frac{x^2}{0.100} = 4.5\times10^{-4}$$

$$x^2 = 4.5\times10^{-5}$$

$$x = 0.0067082039 = [H_3O^+]$$

So, $\boxed{pH = 2.17}$

(Solving the quadratic gives a pH of about 2.19 ...)

Compare:

- Weak acid HNO_2 : pH of 0.10 M solution = 2.17

Let's compare the pH of the weak nitrous acid with the pH of a stopn acid like nitric acid:

0.10 M HNO_3, what is pH?

$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

0.10 M HNO_3, $[H_3O^+] = 0.10$ M

pH = 1.00

The stronger the acid:

- the lower the pH of a solution of given concentration will be
- the higher the concentration of hydronium ion (when compared to the nominal acid concentration)

Consider an 0.100 M solution of the weak base ammonia:

NH_3 ; $K_b = 1.8 \times 10^{-5}$ (p A-14, Ebbing 9th)

What is the pH?

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \boxed{\frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}}$$

We want to solve for HYDROXIDE ion concentration, as it's the only thing in this expression that's related to pH!

Species	[Initial]	Δ	[Equilibrium]
NH_4^+	0	$+x$	x
OH^-	0	$+x$	x
NH_3	0.100	$-x$	$0.100 - x$

$$\boxed{\frac{(x)(x)}{(0.100 - x)} = 1.8 \times 10^{-5}}$$

Solve for 'x' to get hydroxide concentration

$$\frac{(x)(x)}{(0.100-x)} = 1.8\times10^{-5}$$

This is a quadrativ, but we can simplify it to solve faster...

$$\frac{x^2}{0.100-x} = 1.8\times10^{-5}$$

$x \ll 0.100$, so $0.100 - x \approx 0.100$

$$\frac{x^2}{0.100} = 1.8\times10^{-5}$$

Be careful here! We have calculated the HYDROXIDE concentration, not the HYDRONIUM concentration ... so we can't just take the negative logarithm and call it the answer!

$$x = 0.001341608 = [OH^-]$$

$$pOH = -\log_{10}(0.001341608) = 2.87$$

Since $pH + pOH = 14.00$,

$$\boxed{pH = 11.13}$$

* If you'd solved this with the quadratic equation, you would have gotten a pH of 11.13 ... same as this answer.

Compare pH to the pH of an 0.100 M solution of the strong base NaOH:

$pH_{NH_3} = 11.13$

$NaOH \rightarrow Na^+ + OH^-$

So, 0.100 M NaOH, $[OH^-] = 0.100$

$pOH = -\log_{10}(0.100) = 1.00$

$pH = 14.00 - 1.00 = \boxed{13.00}$

The stronger the base:

- the higher the pH will be for a solution of given concentration
- the higher the HYDROXIDE concentration (compared to the nominal base concentration)

Find the pH and the degree of ionization for an 0.10 M solution of formic acid: $HCHO_2$

$$HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$$

$$\boxed{K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]} = 1.7\times10^{-4}}$$

Value of Ka found in Ebbing on page A-13 ...

Species	[Initial]	Δ	[Equilibrium]
H_3O^+	0	+x	x
CHO_2^-	0	+x	x
$HCHO_2$	0.10	-x	0.10-x

$$\frac{(x)(x)}{0.10-x} = 1.7\times10^{-4}$$

$$\frac{x^2}{0.10-x} = 1.7\times10^{-4}$$

If we assume 'x' is small compared to 0.10 ...

$0.10 - x \approx 0.10$

$$\frac{x^2}{0.10} = 1.7\times10^{-4}$$

$$x = 0.00412310 56 = [H_3O^+]$$

So $\boxed{pH = 2.38}$

... But what is DEGREE OF IONIZATION? The fraction of a weak acid (or base) that ionizes in water.

$$\frac{[CHO_2^-]}{[HCHO_2]_{initial}} \approx \frac{[H_3O^+]}{[HCHO_2]_{initial}} = \frac{0.00412310 56}{0.10} = \boxed{0.041 = DOI}$$

Sometimes, we express this in terms of a percentage. We call this PERCENT IONIZATION

$$\%\,\text{ionization} = DOI \times 100\% = \boxed{4.1\%\ \text{ionized}}$$

When you do Experiment 16A. By Le Chateleir's Principle, adding water to the equilibrium should force it to the right - meaning that more acid will ionize - even as the pH goes up!. Therefore, the degree of (or percent) ionization should INCREASES as the concentration of the acid DECREASES. Check this with your experiment 16A data on acetic acid.