

Consider a 0.100M solution of nitrous acid, a WEAK ACID ( $\text{HNO}_2$ )



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

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?

To find pH, we need to know hydronium ion concentration at equilibrium. This time, we can't assume all the acid ionizes. We will have to solve the acid's equilibrium.

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{H}_3\text{O}^+$	0	+X	X
$\text{NO}_2^-$	0	+X	X
$\text{HNO}_2$	0.100	-X	0.100 - X

$$\frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{(x)(x)}{(0.100 - x)} = 4.5 \times 10^{-4}$$

Looks a lot like the equations we solved in Chapter 14!

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

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

Ka is small, so there will be only a small amount of acid ionizing. That means that "x" (which equals the amount of acid that ionizes) is also small.

If x is small compared to 0.100, then ...

$$0.100 - x \approx 0.100$$

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

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

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

$$\text{So, } \boxed{\text{pH} = 2.17}$$

(Solving the quadratic equation gives a pH of 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 is it safe to assume "x" is small enough to drop from the subtraction term? In general, when the acid or base concentration is 1000x or more larger than the value of K

Compare:

- Weak acid  $\text{HNO}_2$  : pH of 0.10 M solution = 2.17

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

0.10 M  $\text{HNO}_3$ , what is pH?



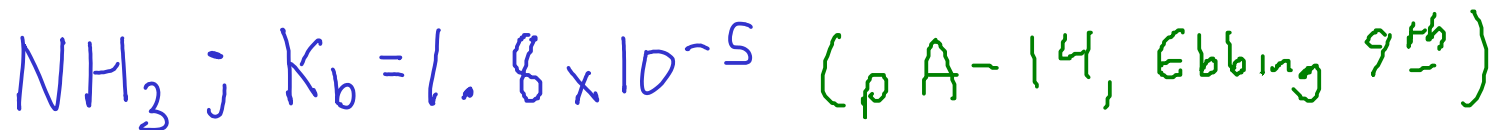
0.10 M  $\text{HNO}_3$ ,  $[\text{H}_3\text{O}^+] = 0.10 \text{ M}$

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)

145 Consider an 0.100 M solution of the weak base ammonia:



What is the pH?



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

We want to find pH. That means we must solve for HYDROXIDE ion concentration, as it's the only thing in this equilibrium that relates to hydronium (and pH) ...

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{NH}_4^+$	0	+x	x
$\text{OH}^-$	0	+x	x
$\text{NH}_3$	0.100	-x	0.100-x

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(x)(x)}{(0.100-x)} = 1.8 \times 10^{-5}$$

Solve for "x" to get HYDROXIDE concentration.

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

This is another quadratic, and can be solved with the quadratic formula. HOWEVER ...

$$\frac{x^2}{0.100-x} = 1.8 \times 10^{-5}$$

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

$$\frac{x^2}{0.100} = 1.8 \times 10^{-5}$$

$$x = 0.0013416408 = [\text{OH}^-]$$

Find pOH first ...

$$\text{pOH} = -\log_{10}(0.0013416408) = 2.87$$

Since  $\text{pH} + \text{pOH} = 14.00$ ,

$$\text{pH} + 2.87 = 14.00$$

$$\boxed{\text{pH} = 11.13}$$

(If you'd solved this problem with the quadratic equation, you'd get a pH of 11.13 ...)

Be careful here! We have calculated the HYDROXIDE concentration (and not the HYDRONIUM concentration). We will need to change to hydronium for the final answer

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

$$\text{pH}_{\text{NH}_3} \approx 11.13$$



$$\text{So, } 0.100 \text{ M NaOH, } [\text{OH}^-] = 0.100$$

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

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

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:  $\text{HCHO}_2$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]} = 1.7 \times 10^{-4}$$

Value from pA-13, Ebbing

We'll solve for hydronium concentration ...

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{H}_3\text{O}^+$	0	+x	x
$\text{CHO}_2^-$	0	+x	x
$\text{HCHO}_2$	0.100	-x	0.100-x

$$\frac{(x)(x)}{(0.10-x)} = 1.7 \times 10^{-4}$$

$$\frac{x^2}{0.10-x} = 1.7 \times 10^{-4}$$

Assume  $x \ll 0.10$ ,  
 $0.10-x \approx 0.10$

$$\frac{x^2}{0.10} = 1.7 \times 10^{-4}$$

$$x = 0.0041231056 = [\text{H}_3\text{O}^+]$$

So,

$$\text{pH} = 2.38$$

... but what about DEGREE OF IONIZATION?

So, what is DEGREE OF IONIZATION? The fraction of a weak acid or base that ionizes in water!

$$\frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]_{\text{initial}}} \approx \frac{[\text{H}_3\text{O}^+]}{[\text{HCHO}_2]_{\text{initial}}} = \frac{0.0041231056}{0.10} = \boxed{0.041 = \text{D.O.I.}}$$

Sometimes, we express this as a percentage:

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

... so about 4 of every 100 formic acid molecules are ionized in this solution. That's what we mean by a WEAK acid!

When you do Experiment 16A. By Le Chateleur'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.