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

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

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

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!

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

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

base ionization constant

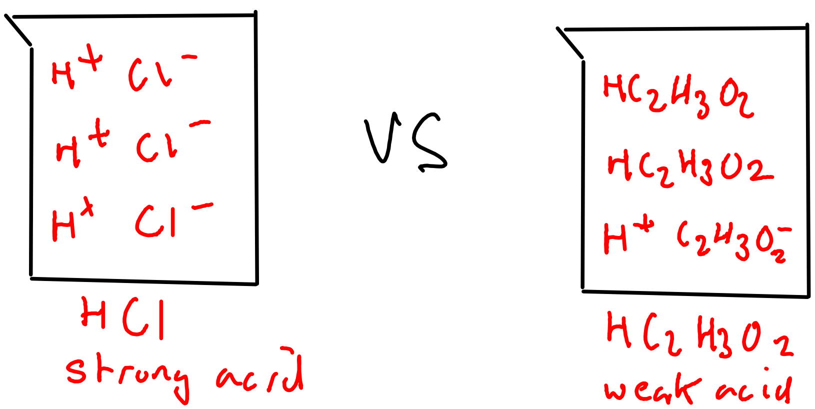
Values for Ka and Kb can often be found in data books / tables / or on the web.

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)

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

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

Values for Ka, like other equilibrium constants, are determined experimentally

What is the pH of the solution?

See pages A-13 and A-14 in your textbook for values for Ka (or use the internet)

To find the pH, we need to find the hydronium ion concentration: $[H_3O^+]$

... so we need to solve the equilibrium expression. We don't know all the equilibrium concentrations, so we try to express them all in terms of a single variable.

SPECIES	INITIAL CONCENTRATION	CHANGE	EQUILIBRIUM CONCENTRATION
H_3O^+	0	$+x$	x
NO_2^-	0	$+x$	x
HNO_2	0.100	$-x$	$0.100 - x$

We assume that the amount of hydronium from the water is small enough to ignore!

Solve in a similar manner to a chapter 14 equilibrium problem!

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

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

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

Quadratic equation:

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

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

IF 'x' is small relative to 0.100, then
0.100 - x approximately equals 0.100

$$0.100 - x \approx 0.100$$

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

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

$$6.71\times10^{-3} = x = [H_3O^+]$$

And $\boxed{pH = 2.17}$

How do we know if it's safe to assume x is small? The assumption is generally safe when the initial concentration and the value of Ka or Kb differ be about a factor of 1000.

Solving the quadratic gives an answer of 2.188 (2.19), which is not very different from the answer we get with our approximation.

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?

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

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

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?

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

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

We need to solve this, BUT which one of these terms are we most interested in?

We will solve for HYDROXIDE concentration, since it's closely related to hydronium - and can be easily converted.

SPECIES	INITIAL CONCENTRATION	CHANGE	EQUILIBRIUM CONCENTRATION
NH_4^+	0	+ X	X
OH^-	0	+ X	X
NH_3	0.100	− X	0.100 − X

Putting these into the equilibrium expression...

$$1.8 \times 10^{-5} = \frac{(X)(X)}{(0.100 - X)} = \frac{X^2}{0.100 - X}$$

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

Like the acid problem we solved earlier, this is a QUADRATIC and can be solved with the quadratic formula. BUT ... we can simplify this one too!

Assume

$0.100 - x \approx 0.100$

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

$0.0013416 = x = [OH^-]$

be careful! This is HYDROXIDE concentration, not HYDRONIUM concentration!

$pOH = -\log_{10}(0.0013416) = 2.87$

$pH + pOH = 14.00$, so

$pH = 11.13$ *

If you'd solved this problem using the quadratic equation, you would have found the pH of the solution to be 11.13.

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 has $[OH^-] = 0.100$

$pOH = -\log_{10}(.100) = 1.00$

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

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)