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

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

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

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

K_a: acid 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!

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

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

K_b: base ionization constant

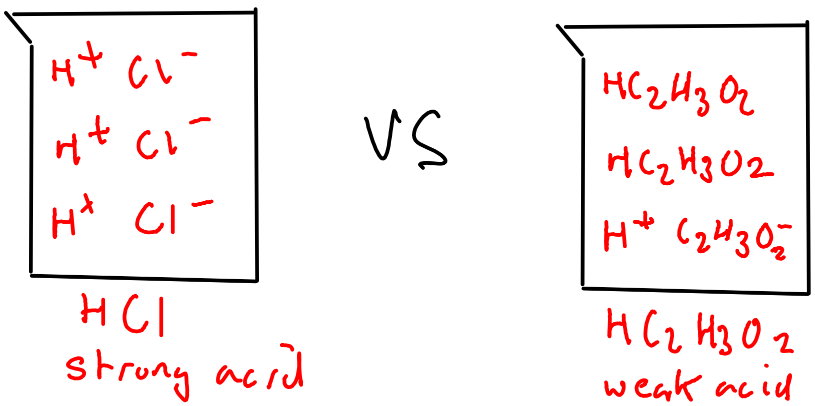
Values for Ka and Kb can often be found in data books / tables / or on the web.

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)

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

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = 5.1 \times 10^{-4}$$

values for Ka are determined experimentally

(We look this number up in a table of acid ionization constants)

What is the pH of the solution?

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

... so we need to solve the equilibrium expression. But we don't know all of the concentrations AT EQUILIBRIUM to do so!

... but they ARE related!

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

SPECIES	INITIAL CONC	CHANGE	EQUILIBRIUM CONC
$[H_3O^+]$	0	$+x$	x
$[NO_2^-]$	0	$+x$	x
$[HNO_2]$	0.100	$-x$	$0.100 - x$

... this is similar to the problems from the equilibrium chapter!

$$5.1 \times 10^{-4} = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

$$5.1 \times 10^{-4} = \frac{(x)(x)}{(0.100 - x)}$$

$$5.1 \times 10^{-4} = \frac{x^2}{0.100 - x}$$

The assumption that x is small relative to the original concentration is usually OK if Ka or Kb is at least 1000 times smaller than the acid or base concentration

Quadratic equation:

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

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

IF x is small relative to 0.1, then 0.1-x approximately equals 0.1

$$0.100 - x \approx 0.100$$

What's this?

For situations where the amount of dissociated acid or base is much smaller than the original amount, it's safe to assume that the concentration of acid or base remains essentially constant at the original amount.

$$5.1 \times 10^{-4} = \frac{x^2}{0.100}$$

$$5.1 \times 10^{-5} = x^2$$

$$7.14 \times 10^{-3} = x = [H_3O^+]$$

So, pH = **2.15** ✗

Solving the quadratic gives a pH of 2.16, which differs by 1 in the last significant figure.

Compare:

- Weak acid HNO_2 : pH of 0.10 M solution = 2.15

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 term are we most interested in?

We want to solve for hydroxide concentation, since it's closely related (and can be easily converted) to pH.

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

Plug in to the equilibrium expression:

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

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

This is a QUADRATIC equation, but like the acid example, x is small compared to 0.100.

$0.100 - x \approx 0.100$

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

$x = 0.001341640\cancel{8} = [OH^-]$

This is HYDROXIDE concentration, not HYDRONIUM. Be careful here!

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

$pH = 14.00 - 2.87$

$pH = 11.13$ *

* If you had solved this by the quadratic equation, you would have obtained a pH of 11.13. (No difference to two significant figures!)

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 bas concentration)