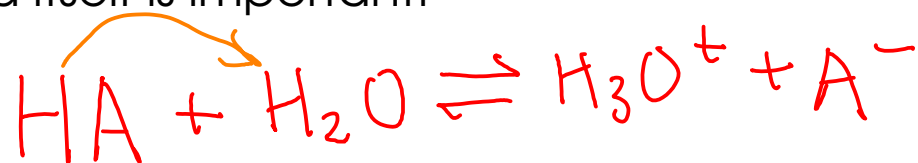For a WEAK ACID, equilibrium does not lie far to the right. The ionization equilibrium of the acid itself is important!
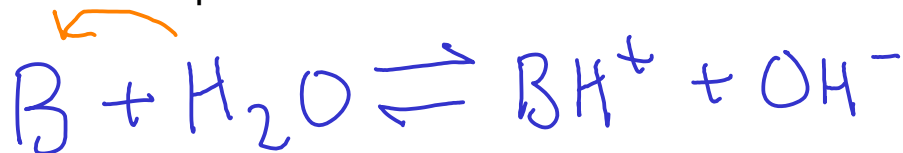
$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

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

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!

H^+ Cl^-
H^+ Cl^-
H^+ Cl^-

HCl
strong acid

VS

$HC_2H_3O_2$
$HC_2H_3O_2$
H^+ $C_2H_3O_2^-$

$HC_2H_3O_2$
weak acid
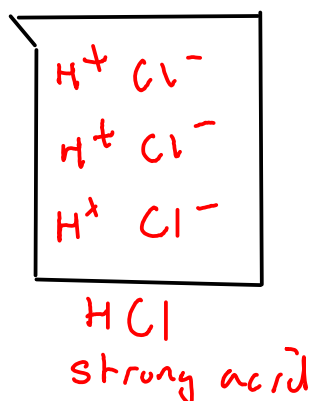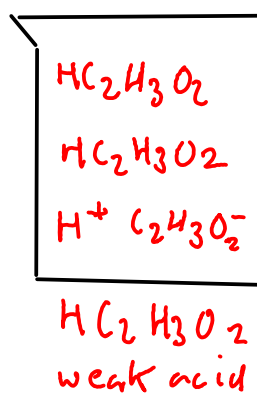
Fewer molecules of the weak acid ionize, so the concnetration of hydrogen/hydronium ion is lower, meaning a higher pH!

- 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 the 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!

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

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

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

Quadratic equation!

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

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

Assume that x << 0.100

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

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

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

$$pH = \boxed{2.15}$$

What's this?
For situations where the amount of dissociated acid or base is much, much smaller than the original amount, it's safe to assume that the amount of undissociated acid remains relatively constant.

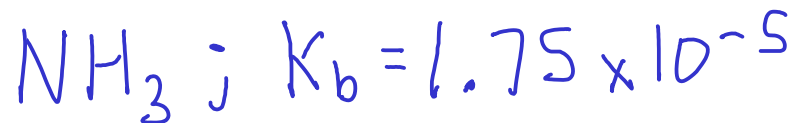In this case, 0.100 - x is essentially the same thing as 0.100 .

... if we'd used the quadratic equation, our answer would have been pH = 2.16

Compare:

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

- Strong acid: pH of 0.10 M solution = 1.00

The stronger the acid, the lower the pH of a solution of given concentration will be!

Consider an 0.100 M solution of the weak base ammonia:

$$NH_3 \; ; \; K_b = 1.75 \times 10^{-5}$$

What is the pH?

$$NH_3 (aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.75 \times 10^{-5}$$

What term in this expression do we actually need to find? We need the HYDROXIDE concentration. It's easily related to HYDRONIUM, which is what we need to know to find the pH!

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

Plug into the equilibrium expression: $$1.75 \times 10^{-5} = \frac{(x)(x)}{0.100 - x} = \frac{x^2}{0.100 - x}$$

$$1.75 \times 10^{-5} = \frac{x^2}{0.100 - x}$$

This is a QUADRATIC EQUATION. But, we expect that the value of 'x' will be much smaller than 0.100. (Look at the equilibrium constant value!) So, we can simplify this problem.

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

$$1.75 \times 10^{-5} = \frac{x^2}{0.100}$$

$0.0013228757 = x = [OH^-]$ HYDROXIDE ion concentration

$-\log_{10}(0.0013228757) = 2.88 = pOH$

$pH + pOH = 14.00$

$pH = 14.00 - 2.88 = \boxed{11.12}$ *

* If you had used the quadratic equation to solve for 'x' in this problem, you would have calculated a pH of 11.12 - no difference from the shortcut (at least, to two significant figures)

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

$pH_{iNH_3} = 11.12$

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

$$[OH^-] = 0.100$$

$$pOH = 1.00$$

$$pH + pOH = 14.00$$

$$\boxed{pH = 13.00}$$

The higher the Ka or Kb value, the stronger the acid or base!

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

$$H(HO_2(aq)) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CHO_2^-(aq)$$

$$K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]} = 1.7 \times 10^{-4}$$

Constant's value at 25 C obtained from chart in textbook, page A-13

SPECIES	(INITIAL)	(CHANGE)	(EQUILIBRIUM)
H_3O^+	0	$+X$	X
CHO_2^-	0	$+X$	X
$HCHO_2$	0.10	$-X$	$0.10-X$

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

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

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

Assume 'x' is much less than 0.10

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

$$x = 0.0041231056 = [H_3O^+]$$

$$pH = -\log_{10}(0.0041231056) = \boxed{2.38 = pH}$$

Degree of ionization? DEGREE OF IONIZATION is the fraction of a weak electrolyte (acid or base) that dissociates in water.

$$\frac{[CHO_2^-]}{[HCHO_2]} = \frac{[H_3O^+]}{[HCHO_2]} = \frac{0.0041231056}{0.10} = \boxed{0.041 = D.O.I.}$$

Sometimes, we express degree of ionization as a percent ... PERCENT IONIZATION

$$\% = D.O.I. \times 100\% = 0.041 \times 100\% = \boxed{4.1\% \text{ ionized}}$$

... so about 96% of this acid exists in solution as undissociated formic acid molecules.

(WEAK acids exist in solution mostly as undissociated molecules!)